GENERAL AND INORGANIC CHEMISTRY

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FOR UNIVERSITY STUDENTS

BY

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PREFACE

THE present book, which is somewhat more advanced than my *Text Book of Inorganic Chemistry for University Students*, is intended to be useful and intelligible to three classes of students. (1) Pupils in higher forms at school and junior students in universities should find most of Part I (General and Physical Chemistry), except some advanced sections, suitable as an introduction to this subject, in particular for scholarship examinations, and many sections of Part II (Inorganic Chemistry) should be of interest to them. (2) Degree students will find all the Inorganic Chemistry they require in the book; they can omit some sections on the rarer elements, the general summaries at the heads of the chapters giving most of the information on these which they require. (3) For Honours students the whole book should serve as a companion to their studies; the more advanced subjects, or those which they need to know in more detail, are best read in original papers or other such sources, many references to which are given. It has been possible, by careful selection, and a uniform and concise method of treatment, to present a good deal of material in a book of moderate size.

The elements are dealt with in the order of the groups in the Periodic Table, non-metals and metals being taken together. This plan has been criticised as tending to over-emphasise some less important analogies and under-estimate some important differences, but no two authors who prefer other arrangements, whether based on electro-chemical properties, valency, isomorphism or the supposed best order for teaching, agree in this order. The teacher can easily change the order as he wishes, since all the chapters are self-contained, and he can also deal with the non-metals and metals separately.

In the study of individual metals the order of anion elements is that of the Periodic Table, except that halides (group VII) usually precede oxides (group VI), for the reason that the former are usually soluble and the latter not, so that the cation properties, which are the most important in the study of the metal, come first. A treatment which goes back to Berzelius and became traditional among some London teachers (Graham, Fownes, Ramsay) grouped the metal salts under anions (acid radicals), the carbonates, nitrates, sulphates, etc., being taken together. This has a disadvantage in that the individual properties depend much more on the cation than on the anion. Some groups of closely related compounds, such as the sulphates of bivalent copper, zinc, manganese and iron, depend for their similarity on the valency-state of the cations, and not on the identity of anion. Such resemblances should be noted by the teacher and student, but do not seem to call for the grouping of salts under the anions.

The second part of the book dealing with elements and compounds necessarily includes much that the student will not have learned in school. Many unfamiliar substances are described, and the student may wonder whether some kind of generalisation could not be attempted, which would spare him the

necessity of studying all these individual substances. To this suggestion there are several replies.

First, only a small fraction of Inorganic Chemistry can be comprised in a few hundred pages. The " Treatise " of Mellor, for example, contains over 15,000 closely printed pages and is incomplete ; many new discoveries have been made since it was published. The information now presented is thus a very condensed and critical selection. Secondly, it is impossible to make useful generalisations unless the individual facts on which they are based are known : a mere study of the Periodic Table, for example, would convey nothing without a knowledge of the individual elements. Finally, a student preparing to be a chemist must realise that a knowledge of generalities, giving some notion of the scope and spirit of Chemistry, is insufficient for a specialist. The book is intended for students who are keenly interested in Chemistry.

Chemistry has progressed by becoming more and more quantitative. The physical constants for many substances are given in the book and are often collected in tables which give a concise view of groups of related substances. A student is not expected to remember these constants. They are useful in laboratories where large tables are not available, and have been critically selected. A chemist should know, without constant reference to tables, the general physical properties of substances ; that bromine, for example, is a liquid heavier than water and sulphuric acid, but not so dense as mercury, and it would be impossible to convey such information without figures. These numbers should, in fact, be *read* with the text, and the student encouraged to take an interest in them. The author has the impression that the American student is more interested in facts and numbers than the English student, and this taste and habit of mind is one which can with profit be encouraged and developed. A knowledge of the *approximate* values of some important constants, such as the electronic charge, Avogadro's number, the gas constant, the order of atomic dimensions, and Planck's constant, is also very useful. In the author's experience students begin to take a more active interest in the theories when their attention is directed to such numerical values.

Experiments for lecture demonstration are described in sufficient detail to enable them, after suitable trial, to be carried out with success : some books on lecture experiments are quoted after the preface. Details of technical processes are not usually given, but enough is said to indicate which reactions are carried out on the large scale, and their relative importance ; many students think that the arc process for the fixation of nitrogen is important but the sulphuric acid chamber process obsolete, whereas the opposite is true. Only modern processes are described, except when an old process has some scientific interest, *e.g.* the Deacon process for chlorine, or the Leblanc alkali process. Some new patent specifications relate to obsolete processes which have again come into prominence, and the operation of a technical process often depends more on economic conditions than on its suitability on other grounds.

Many references to original papers and other sources are given, and in other cases authors and dates of publication are stated, from which the original can easily be found from abstracts. The names of journals are abbreviated in

accordance with the list which follows the preface. I have always attached importance to students consulting some original papers, and agree with the remarks of George Fownes in the preface to his very successful *Manual of Chemistry*, which first appeared in 1847 and reached a fourteenth edition in 1889 : his words are regarded as describing the aim of the present book :

> " The work has no pretensions to be considered a complete treatise on the subject, but is intended to serve as an introduction to the larger and more comprehensive systematic works in our own language and in those of the Continent ; especially to prepare the student for the perusal of original memoirs, which, in conjunction with practical instruction in the laboratory, can alone afford a real acquaintance with the spirit of research and the resources of Chemical Science."

I have tried to avoid a narrow and prejudiced outlook, and hope that readers will use many alternative sources of information. They will come across many contradictions and discrepancies, and if they take the trouble to find out which statements in their reading are merely erroneous (since every author is liable to error), and which are still uncertain, and what reasons there are for preferring one to another, they will gain something of value. This procedure has been followed in the preparation of the book, and in many cases several original papers had to be consulted before a small portion of text could be written. No virtue is claimed for this ; an author is expected to take pains in his work, although he may not always do so.

The question of nomenclature, or the naming of compounds, is one which offers some difficulty in Inorganic Chemistry. The main principles laid down in 1787 by Lavoisier and his colleagues * are still followed, but in contrast with Organic Chemistry there is some diversity, which should not be regarded as undesirable. The proposals made † for a uniform nomenclature were carefully considered, and not all of them were found acceptable. The name *halides* is preferred to *halogenides*, since it is shorter and in conformity with usage in Organic Chemistry. (The name *chalkogenides* for sulphides, selenides and tellurides is not used.) In general, the names of complex salts are based on those of oxy-salts in which an element has the same valency, *e.g. fluosilicates* rather than *silicofluorides*. In the case of complex cyanides, however, the well-established names *ferrocyanide* and *ferricyanide* are used instead of *cyanoferrite* and *cyanoferrate* ; partly because there is disagreement in the naming of the oxy-salts, which could lead to confusion, and partly because, if this system is carried out logically, such names as *cyanoargentite* for salts of $Ag(CN)_2$ would have to be used in cases where no oxy-salts are known or even expected. One recommendation deliberately rejected is that of naming compounds after the supposed valency of the element, ferrous and ferric chlorides being called *iron* II *chloride* and *iron* III *chloride*, etc. This seems objectionable, partly because the valency is not always certain, and more particularly because it leads

* *Méthode de Nomenclature Chimique*, by Lavoisier, Berthollet, Fourcroy, and Guyton de Morveau, 1787 ; the system originated with the last named.

† *J.C.S.*, 1940, 1404 ; *Chem. Reviews*, 1943, **32**, 73 ; the valency method originated with Stock.

to errors; the German name "Iridium IV Oxyd", for example, has been translated "iridium tetroxide" in Mellor's "Treatise", and the compound described as IrO_4, whilst it is actually the dioxide IrO_2 of supposedly 4-valent iridium.

It now only remains for me to thank those who have, in various ways, assisted me in the preparation of the book. Dr. W. G. Palmer, of the University of Cambridge, read Part I in manuscript and also allowed me to use some of the illustrations in his own excellent book.* My former student, Mr. S. K. Tweedy, B.Sc., worked the numerical examples in the first part of the book, correcting not a few errors in the original sources from which they were taken. Mr. A. F. J. Light prepared the drawings for some new illustrations. Sir Richard Gregory, Bart., F.R.S., read the proofs, and placed his kind encouragement and wise counsel at my disposal. The publishers, Messrs. Macmillan, gave me all possible help in the preparation of the illustrations, and met my wishes in deciding the size and scope of the book.

CAMBRIDGE, *March*, 1944. J. R. PARTINGTON

* *Experimental Physical Chemistry*, Cambridge, 1941.

CONTENTS

List of Reference Abbreviations

Amer. Chem. J. : American Chemical Journal, Baltimore, 1879–1913.
Annalen : Annalen der Chemie (" Liebig's Annalen "), Leipzig, 1832– .*
Ann. Chim. : Annales de Chimie, Paris, 1789– .
Ann. Physik : Annalen der Physik, 1799– .
Ann. Rep. C.S. : Annual Reports of the Chemical Society (London), 1904– .

Ber. : Berichte der Deutschen Chemischen Gesellschaft, Berlin, 1868– .
Bull. Bur. Mines : U.S. Bureau of Mines Bulletin, Washington, 1910– .
Bull. Soc. Chim. : Bulletin de la Société Chimique de France, Paris, 1858– .

Canad. J. Res. : The Canadian Journal of Research, 1929– .
Chem. Abstr. : Chemical Abstracts, (i) British, issued by the Chemical Society (London), section *A* (Pure Chemistry), 1926– ; (ii) American, issued by the American Chemical Society.
Chem. Met. Eng. : Chemical and Metallurgical Engineering, New York, 1902– . (Has had the titles : Electrochemical Industry, 1902–4, Electrochemical and Metallurgical Industry, 1905–9, Metallurgical and Chemical Engineering, 1910–18).
C. S. Faraday Lectures : Faraday Lectures, Chemical Society (London) 1928.
C. S. Memorial Lectures : Memorial Lectures, Chemical Society (London), 3 vols., 1901–14–33.
Chem. N. : The Chemical News, London, 1859–1932.
Chem. Rev. : Chemical Reviews, Baltimore, 1924– .
Chem. Zentr. : Chemisches Zentralblatt [formerly Centralblatt], Berlin, 1856– (the most complete abstract collection).
Chem. Ztg. : Chemiker-Zeitung, Cöthen, 1879– .
Chim. et Ind. : Chimie et Industrie, Paris, 1918– .
College Course : Partington, " College Course of Inorganic Chemistry," 1939.
Compt. Rend. : Comptes rendus hebdomadaires des séances de l'Académie des Sciences, Paris, 1835– .

Gazz. : Gazzetta Chimica Italiana, Rome, 1871– .

Ind. Eng. Chem. : Industrial and Engineering Chemistry, 1909– (issued by the American Chemical Society).

J.A.C.S. : Journal of the American Chemical Society, Washington, 1879– .
J.C.S. : Journal of the Chemical Society (London), 1849– .
J. Chem. Phys. : Journal of Chemical Physics, 1933– .
J. Chim. Phys. : Journal de Chimie Physique, Paris, 1903– .
J. Franklin Inst. : Journal of the Franklin Institute, Philadelphia, 1825– .
J. Phys. Chem. : Journal of Physical Chemistry, Ithaca, New York, 1896– .
J. Res. Bur. Stand. : Bureau of Standards Journal of Research, Washington, 1929– .
J.S.C.I. : Journal of the Society of Chemical Industry, London, 1881– . (In 1918 a section was called Review (R), in 1923 Chemistry and Industry, other sections being the Transactions (T) and Abstracts (A), the last issued from 1926 as Section B of British Chemical Abstracts ; from 1944 Chemistry and Industry appeared without volume number).

* A hyphen indicates that publication is still in progress.

Manch. Mem. : Memoirs and Proceedings of the Literary and Philosophical Society, Manchester, 1789– .
Mem. C. S. : Memoirs and Proceedings of the Chemical Society (London), 1841–48.
Monatsh. : Monatshefte für Chemie und verwandete Theile anderer Wissenschaften, Vienna, 1881– .

Nature, London, 1870– .

Phil. Mag. : Philosophical Magazine, London, 1798– .
Phil. Trans. : Philosophical Transactions of the Royal Society of London, 1665– ; after 1886 a B series (biological) appeared in addition to the A series (to which alone reference is made).
Phillipine J. Sci. : The Phillipine Journal of Science, Manila, 1906– .
Phys. Rev. : The Physical Review, Minneapolis, 1894– .
Proc. C. S. : Proceedings of the Chemical Society (London), 1885–1914.
Proc. Nat. Acad. Sci. : Proceedings of the National Academy of Science, Washington, 1915– .
Proc. Roy. Soc. : Proceedings of the Royal Society, London, 1856– .
Proc. R. S. Edin. : Proceedings of the Royal Society of Edinburgh, 1845– .

Rec. Trav. Chim. : Recueil des travaux chimiques des Pays-Bas, Leiden, 1882– .

School Course : Partington, " A School Course of Chemistry," 1934.
Science Progress, London, 1894– .

Trans. Amer. Electrochem. Soc. : Transactions of the [American] Electrochemical Society, New York, 1902– .
Trans. Faraday Soc. : Transactions of the Faraday Society, London, 1905– .

Z. angew. Chem. : Zeitschrift für angewandte Chemie, Leipzig, 1894– .
Z. anorg. Chem. : Zeitschrift für anorganische Chemie, Leipzig, 1892– .
Z. Elektrochem. : Zeitschrift für Elektrochemie, Leipzig, 1895– .
Z. Phys. : Zeitschrift für Physik, Berlin, 1920– .
Z. phys. Chem. : Zeitschrift für physikalische Chemie, Leipzig, 1887– (since 1928 divided into an A and B series, only the A being referred to in this book).

List of Works of Reference

A. *Large Handbooks or Dictionaries.*

Abegg, Handbuch der anorganischen Chemie, Leipzig, 1908– .
Berzelius, Traité de Chimie, 2nd French edit., Paris, 1845–50.
Dammer, Handbuch der anorganischen Chemie, Stuttgart, 1892–5.
Fremy, Encyclopédie Chimique, Paris, 1882– .
Friend, J. N., Text Book of Inorganic Chemistry, 1914– .
Gmelin, Hand Book of Chemistry, English transl. by H. Watts, 1848–72 ; several German editions, the last, Gmelins Handbuch der anorganischen Chemie, 8th edit., Berlin, 1926– ; the most compendious work on Inorganic Chemistry.
Hoffmann, M. K., Lexicon der anorganischen Verbindungen, Leipzig, 1912–19 (a list of compounds, with references).
Mellor, A Comprehensive Treatise on Inorganic and Theoretical Chemistry, 16 vols., 1922–37 (the most compendious work in English).
Moissan, Traité de Chimie Minérale, Paris, 1904– .
Pascal, Traité de Chimie Minérale, Paris, 1931–34.

Roscoe and Schorlemmer, Treatise on Chemistry, vol. 1 (non-metals), 1920; vol. 2 (metals), 1923.
Thorpe, Dictionary of Applied Chemistry, new edit., 1937– .
Ullmann, Enzylopädie der technischen Chemie, 2nd edit., Berlin, 1928–32.
Watts, Dictionary of Chemistry, and Supplements, 1872–81; new edit. by Morley and Muir, 1890–94.
Wurtz, Dictionnaire de Chimie, and Supplements, Paris, 1869– .

B. *Smaller Text Books.*

Bloxam, Chemistry, Inorganic and Organic, 1867; 11th edit. 1923.
Emeléus and Anderson, Modern Inorganic Chemistry, 1939.
Ephraim, Text Book of Inorganic Chemistry, 4th edit. 1943.
Hofmann, K. A., Lehrbuch der anorganischen Chemie, 7th edit., Brunswick, 1931.
Mendeléeff, The Principles of Chemistry, 3rd edit., 2 vols., 1905.
Morgan and Burstall, Inorganic Chemistry, 1936.
Remy, Lehrbuch der anorganischen Chemie, 2 vols., Leipzig, 1931–2.
Riesenfeld, Lehrbuch der anorganischen Chemie, 2nd edit., Vienna, 1939.

C. *Books with Descriptions of Experiments.*

Arendt and Doermer, Technik der anorganischen Experimentalchemie, Hamburg and Leipzig, 1910.
Arthur, Lecture Experiments in General Chemistry, New York, 1939.
Biltz, Laboratory Methods of Inorganic Chemistry, New York, 1928.
Fowles, Lecture Experiments in Chemistry, 1937.
Frankland, How to Teach Chemistry, 1875.
Goddard, Fundamental Experiments in Chemistry, n.d.
Gorup-Besanez, Lehrbuch der anorganischen Chemie, 7th edit., Brunswick, 1885.
Heumann, Anleitung zum Experimentieren bei Vorlesungen über anorganische Chemie, Brunswick, 1876.
King, Inorganic Preparations, 1936.
Newth, Chemical Lecture Experiments, 1915.

INTRODUCTION

CHEMISTRY has developed from an early period, although it is only during the last century and a half that it has taken its modern shape. It is not without interest to trace its development, since in this way the reason for many of its modern features becomes clear.* It has been remarked that a science usually reaches its simplest concepts by the most difficult and least direct way, and Chemistry is no exception.

The views of the early Greek philosophers on the nature of matter, as codified by Aristotle (384–322 B.C.), assume that all bodies are composed of the same primary matter (*hulē*) on which a different form (*eidos*) is impressed to give each individual body. Aristotle combined some older Greek theories into the theory of the *four elements*: fire, air, water and earth, giving an order of increasing density. These were supposed to be inter-convertible, and they really represented fundamental *properties* of matter, of which every body partook in some degree. These fundamental properties were supposed to be heat and cold, moistness and dryness, water being cold and moist, earth cold and dry, etc.

Aristotle would have been greatly interested in the modern theory in which the properties of a substance are related to the arrangement (*eidos*) of primary particles (protons, neutrons, electrons) in an atom; at present more than one primary matter (*hulē*) is still necessary. His master, Plato, would have found more congenial the order of the Periodic Table, with its ultimate origin in a property of numbers (Pauli's principle, p. 257), and the large part which mathematics (wave mechanics, quantum theory) plays in Chemistry.

The theory of primary matter led to the view put forward in Greek treatises composed from the first century A.D., probably at Alexandria in Egypt, that metals can be transmuted into gold by means of some agent, later called the *elixir* or the philosophers' stone. Copper could be converted into a white alloy resembling silver by treatment with arsenic, and so on, the process being compared with dyeing. This led to *Alchemy* (the name being formed from the Arabic article *al* and the Greek name *chemia*, χημεία, apparently derived from the old name, *Chemi*, for Egypt).

Alchemy, although long discredited, and unsuccessful with the limited means of experiment available, now has an experimental justification, and the transmutation of the chemical elements is an accomplished fact (p. 205). Lead and mercury, regarded by the alchemists as most nearly related to gold, are the two common metals which stand closest to it in atomic mass and atomic structure (p. 263).

Alchemy was cultivated by the Arabs, who developed the theory that metals contain a principle, "mercury," giving them their metallic properties, and a principle of combustibility, "sulphur," which gives them their colours

* Partington, *A Short History of Chemistry*, 2nd edit., 1939.

and special properties, in particular that of being turned to drosses or calces (Latin *calx*, lime) by roasting in air.

These views persisted until the close of the seventeenth century, although they had been called into question, on the basis of experiment, by Van Helmont (1577–1644), who regarded water as the primary matter.* A third principle was added to the mercury and sulphur of the Alchemists by Paracelsus (1493–1541),† viz. salt, which represents the properties of fixity and solubility.

In 1661 Robert Boyle, in his *Sceptical Chymist*, argued that Aristotle's four elements : fire, air, water and earth, and the three alchemical principles : salt, sulphur and mercury, are not true constituents of bodies, these being rather : " the ingredients of which perfectly mixt bodies [*i.e.* compounds, as distinguished from mechanical mixtures] are immediately compounded and into which they are ultimately resolved." The simple bodies are discoverable by experiment and are the ultimate terms of the analysis of substances. With the working out of this idea, Chemistry became a true science, since such a limitation of its aims was a necessary preliminary stage in its development.

The earliest theory of Chemistry which was based on experiment was the *Phlogiston Theory*,‡ vaguely expressed by J. J. Becher in 1669, and clarified and elaborated by G. E. Stahl in the opening years of the eighteenth century. This assumed that metals are composed of their calces (*i.e.* what we now call oxides) and an inflammable or fiery principle, *phlogiston* (Greek, *phlox*, flame), also present in large amount in combustible bodies such as oils and charcoal, and transferable from one body to another, so that phlogiston lost by calcining a metal could be restored by heating the resulting calx (regarded as an element) with a combustible body. Similarly, sulphur was regarded as a compound of the element sulphuric acid and phlogiston.

Lavoisier,§ using and extending experimental material accumulated by Boyle, Hooke, Mayow, Black, Scheele, Cavendish, and Priestley, showed in 1775-80 that combustion and calcination do not involve the loss of an inflammable principle, phlogiston, but rather the combination of the combustible or metal (which are chemical elements in Boyle's sense) with *oxygen*, a gaseous constituent of the atmosphere, with the formation of acids and bases (metal oxides), respectively. To explain the evolution of heat and light in combustion, Lavoisier brought in a hypothetical imponderable element (*i.e.* one without weight), which he called *caloric*, and this in many ways resembled the old phlogiston.

Lavoisier's theory was incomplete until Cavendish's experiments, published in 1784, showed that water is formed by burning hydrogen in oxygen. This contradicted Lavoisier's idea that a non-metal combining with oxygen gave an acid, since water is neutral. It explained the evolution of an inflammable gas (hydrogen) when metals dissolve in acids, this gas having been identified by some chemists with phlogiston, derived from the metal.

* Partington, *Annals of Science*, 1936, **1**, 359.

† Titley, *Ambix*, 1938, **1**, 166 ; Partington, *Nature*, 1941, **148**, 332.

‡ Partington and McKie, *Annals of Science*, 1937, **2**, 361 ; 1938, **3**, 1, 337 ; 1939, **4**, 113.

§ Hartog, *Annals of Science*, 1941, **5**, 1 ; Partington, *Nature*, 1943, **152**, 207.

The study of acids, bases and salts from the seventeenth century formed an important branch of Chemistry outside the subject of combustion.* Quantitative experiments on the composition of salts were made in the second half of the eighteenth century by Bergman, Wenzel, Richter and others; and Richter, on the basis of experiments, announced the law of equivalent proportions in 1792.

The facts of combining proportions received an explanation in the atomic theory of John Dalton (1803; first published in 1807), which is so simple that, as Lothar Meyer said, "at first sight it is not illuminating." The atomic structure of matter is an old Greek hypothesis, proposed by Leukippos and Demokritos about 450 B.C., but rejected by the schools of Plato and Aristotle on what seemed indubitable logical grounds. It was only about 1650 that it became prominent in science; Newton made use of it, and from him Dalton took it and made it the basis of Chemical Philosophy.† The theory is now paramount in all branches of exact science. Elements are composed of atoms of definite weight, and compounds are formed from elementary atoms in fixed whole-number ratios; the discovery that elements may be mixtures of atoms of different weight, the so-called *isotopes*, is a later development (p. 185).

The determination of the combining proportions of the elements is not in itself sufficient to give the relative weights of the atoms. How this can be done was first explained by Avogadro in 1811, but his hypothesis was not systematically used until Cannizzaro in 1858 showed how it could be applied in determining a uniform system of atomic weights. The determination of molecular weights from gas or vapour densities, explained by Avogadro, was extended to the determination of the molecular weights of substances in solution from freezing points, etc., by Raoult from 1882, and in 1886 van't Hoff enunciated the so-called "gaseous theory of solutions," in which the close relation between the physical properties of dilute solutions and those of ideal gases was emphasised, the osmotic pressure of a solution being analogous to the pressure of a gas.

The examination of the relations among the atomic weights of the elements led Mendéleeff in 1869 to the *Periodic Law* (p. 172), which not only provided a means of classification of the elements superior to any previously used, but also focused attention on relations between atomic weights which in course of time led to important developments in the atomic theory. The Periodic Table is the key to the inner meaning of the properties of the chemical elements.

Chemical reactions were explained from the end of the seventeenth century (Mayow, 1674) by postulating an attractive force, *elective affinity*, having varying intensities, so that if a substance A has a stronger attraction for another B than a third C has, then, according to Bergman (1775), A will displace C completely from the compound BC by the reaction $A+BC=AB+C$. Berthollet (1801–3) opposed this idea and emphasised the incomplete character of many reactions, a state of *equilibrium* being set up in which B is shared between A and C in a ratio depending on the relative *active masses* (concentrations) of A and C competing for B: $A+BC \rightleftharpoons AB+C$. This effect, called *mass action*,

* Marsh, *The Origin and Growth of Chemical Science*, 1929.

† Partington, *Annals of Science*, 1939, **4**, 245.

was not generally recognised, mainly because Berthollet included solutions as compounds of variable composition, whilst Dalton's atomic theory required that a true compound should have a fixed composition. The correct quantitative statement of the law of mass action by Guldberg and Waage (1867) led to the general adoption of the law, which forms an important part of modern Chemistry (Chap. V).

Lavoisier's view that acids are compounds of non-metals with oxygen, and bases compounds of metals with oxygen, was extended by Berzelius from 1811 into a *Dualistic System*. Salts are binary compounds of acids and bases (really acidic and basic oxides) :

sulphuric acid	= sulphur + oxygen	(SO_3)
potash	= potassium + oxygen	(K_2O)
sulphate of potash	= sulphuric acid + potash	($SO_3 + K_2O$).

The dualistic formulation of salts of oxy-acids has persisted in calculations of titrations with oxidising agents such as permanganate and dichromate, formulated as K_2O,Mn_2O_7 and $K_2O,2CrO_3$, the higher oxides being reduced to MnO and Cr_2O_3, and a ferrous salt, *e.g.* FeO,SO_3, being oxidised to a ferric salt, *e.g.* $Fe_2O_3,3SO_3$. It also has some advantage as a basis for the systematic classification of oxysalts.* In particular, many formulae of silicates (*e.g.* felspar, $K_2O,Al_2O_3,6SiO_2$) and complex acids and their salts (*e.g.* ammonium phosphomolybdate, $24MoO_3,P_2O_5,5(NH_4)_2O,20H_2O$) are still written in dualistic form, as are formulae for double salts such as alum, $K_2SO_4,Al_2(SO_4)_3,24H_2O$, and, in general, compounds the exact structure of which is still doubtful.

Chemical symbols and formulae in their present form were proposed by Berzelius in 1813. He represented an atom of an element by a letter symbol, an atom of oxygen being represented by a dot placed over the symbol. With his system of atomic weights :

$$\left.\begin{array}{l}\text{sulphuric acid} = S + 3O = \dddot{S} \\ \text{potash} \quad\quad = K + O = \dot{K}\end{array}\right\} \text{sulphate of potash} = \dot{K} + \dddot{S}$$

Chemical notation is much more systematic and perspicuous than that of other sciences. Berzelius retained Lavoisier's caloric, or the matter of heat and light, as an imponderable element, and added electricity and magnetism to this group.

The researches of Davy, leading to the isolation of the alkali metals in 1807, had shown the importance of electricity in chemical reactions, and the binary character of compounds expressed in the Dualistic Theory was linked by Berzelius with the electric polarity of positive and negative charges in his *Electrochemical Theory* (p. 97) ; the two parts of a compound are positive and negative. Oxygen was always electronegative, metals electropositive ; other elements could be sometimes relatively positive (as sulphur in $SO_3 = \overset{+}{S} + 3\overset{-}{O}$), or sometimes negative (as sulphur in $\overset{+}{Cu} + \overset{-}{S}$), depending on the strength of

* Ramsay, *System of Inorganic Chemistry*, 1891 ; Abegg, *Z. phys. Chem.*, 1909, **69**, 1.

electrochemical character of the other element with which they are combined. The bases are the positive and the acids the negative components of salts : $(\dot{K})^+ + (\dot{\dot{S}})^-$.

Electrochemical Dualism had its experimental foundation on the facts of electrolysis. Hydrogen, alkalis, earths, and metals go to the negative pole and were assumed to be positive ; oxygen, acids, and oxidised compounds go to the positive pole, and were assumed to be negative.

The proof by Davy in 1811 that chlorine is not a higher oxide of an unknown non-metallic element, " murium," but an element, muriatic acid being a compound of it with hydrogen, showed that the Lavoisier-Berzelius theory of acids as oxides of non-metals is too narrow. It was only after a period of some years that Berzelius could accept Davy's view. Wöhler says that in 1823 Berzelius's cook, Anna, was washing some apparatus in his kitchen-laboratory, and said a flask smelled of oxymuriatic acid. " Call it chlorine, Anna, that is better," said Berzelius, to the surprise of Wöhler.

Chlorine is also an " oxidising agent," and it became evident that a whole group of reactions called " oxidations " did not really involve oxygen at all as an essential partner. In the ionic theory (p. 101) " oxidation " is equivalent to the increase of positive charge of a charged particle or ion, or to loss of negative charge, and after the discovery that negative electric charge is composed of particles, *electrons*, of very small mass, negligible in comparison with the masses of the reacting atoms, it was seen that " oxidation " is really the result of loss of electrons. Thus, if the old weightless phlogiston is identified with the nearly weightless electron, the two theories are strikingly alike : *

old theory : oxidation = loss of phlogiston
new theory : oxidation = loss of electrons.

A metal, in the new theory, is composed of metal ions (*i.e.* its oxidised form) and free electrons ; if the electrons are removed, the metal is oxidised. The electrons may be removed by combining with oxygen atoms to form negatively charged oxygen ions, so that the oxide contains positive metal ions (already present in the metal) and negatively charged oxygen ions. The electrons, however, can just as well convert some other element, such as chlorine, into negative ions, and oxygen is not essential to oxidation, being merely one possible medium for the removal of electrons.

Physics and Chemistry have long been closely related. When heat, light, electricity and magnetism were regarded as imponderable elements, their study belonged to Chemistry ; many fundamental discoveries in these fields were made by chemists. When energy was recognised as a real entity, about the middle of the nineteenth century, the study of these subjects was transferred to Physics, previously concerned mostly with dynamics. Chemical Physics, or Physical Chemistry, continued to form part of Chemistry, and, for reasons outlined above, Electrochemistry was an important part of this border-line study. This received a powerful impetus with the formulation by Arrhenius, in 1887, of the

* Partington, *Scientia*, 1938, **64**, 121.

theory of *electrolytic dissociation*. The notion that salts in solution are broken down into charged ions was startling, but as time went on it became clear that even the solid salt is an aggregate of charged ions, a crystal of common salt, for example, being an ordered *lattice* of sodium and chlorine ions, Na^+ and Cl^-, and not of sodium chloride molecules, NaCl, which probably have no existence. This picture, given in the older crystallographic theories, has received confirmation by the newer X-ray method of investigation. This necessarily led to modifications of the view of electrolyte solutions, and the theory of Debye and Hückel (1923), with necessary extensions, is the basis of the modern theory.

The changed outlook also required a modification in the application of the law of mass action to electrolytes; this is most conveniently brought in by the use of *activities* in place of concentrations, since these arise naturally in the thermodynamic treatment, which is beyond the scope of the present book. It is very desirable that a student should become acquainted with the modern theory at an early stage, and this should present no difficulties, provided the matter is presented in an elementary way. The content of Chapter VI forms an important part of modern day-to-day laboratory technique, and much of it is quite intelligible and interesting to relatively elementary students.

About 1830 the great activity in the investigation of carbon compounds, which was to continue with ever-growing speed and intensity through the rest of the century, was beginning to make itself felt. Until then the few organic compounds known could be assimilated into the Dualistic System by the assumption that they were binary compounds of organic *radicals*, the latter behaving in some ways like the elements of inorganic compounds. Berzelius, for example, regarded alcohol as the oxide of a radical C_2H_6, *i.e.* as $C_2H_6 + O$, ether as the oxide of another radical C_4H_{10}, *i.e.* as $C_4H_{10} + O$, and acetic acid as the trioxide of a radical C_4H_6, *i.e.* as $C_4H_6 + 3O$ (this being really the formula of the then unknown anhydride, $C_4H_6O_3 = 2C_2H_4O_2 - H_2O$). The radicals themselves could never contain oxygen.

Wöhler and Liebig in 1832 showed, however, that a whole group of compounds could be regarded as derived from an oxidised radical benzoyl, $C_{14}H_{10}O_2 (= 2C_6H_5CO)$, and in 1838 Dumas found that the supposedly positive hydrogen in acetic acid $C_2H_4O_2$ could be partly replaced by supposedly negative chlorine, without any great change in chemical properties, the resulting trichloracetic acid, $C_2HCl_3O_2$, being very like acetic acid.

Dumas thus proposed a *Unitary Theory*, which regarded a molecule as a complete whole, not a dualistic compound of two parts of opposite electric charge; and in this complete whole or unit, parts could be replaced by *substitution* by other elements, irrespective of their supposed electrochemical characters. Acetic acid, $C_2H_4O_2$, could have three atoms of hydrogen replaced by three atoms of chlorine without essential change of properties.

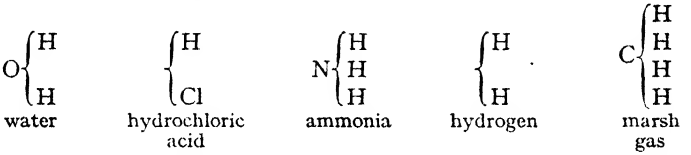
Berzelius could not admit this restriction of the Dualistic Theory, and he attempted to include acetic and trichloracetic acids in its general plan by giving them different formulae, acetic acid being hydrated trioxide of acetyl, whilst trichloracetic acid was a compound of hydrated oxalic acid, $C_2O_3 + H_2O$, with

carbon chloride C_2Cl_6, the latter being " copulated " to the oxide of carbon so as not to alter the essential character of the acid :

acetic acid $(C_4H_6 + 3O) + H_2O$
oxalic acid $C_2O_3 + H_2O$
trichloracetic acid $(C_2O_3 . C_2Cl_6) + H_2O$.

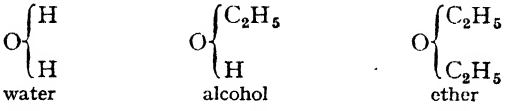
Although the *Radical Theory* was shown by the later researches of Frankland and Kolbe, Bunsen, and others, to be capable of extension, and is still an integral part of modern Organic Chemistry, the intensive study of substitution reactions by Dumas, Laurent, and Gerhardt, focused attention on an essential weakness of the Dualistic Theory, and by about 1840 this had largely fallen into discredit.

The Unitary Theory soon changed into a formal scheme known as the *Theory of Types*. Gerhardt in 1853 proposed four types, into which all compounds were forced by substitution reactions, and Kekulé added another, that of marsh gas (CH_4), in 1857 :



Acetic acid and trichloracetic acid were represented on the type theory by the formulae :

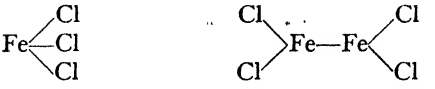
hydrogen in the acetyl radical C_2H_3O being substituted by chlorine. The water type had already been proposed by Williamson in 1850, who had shown that alcohol and ether both belong to it :



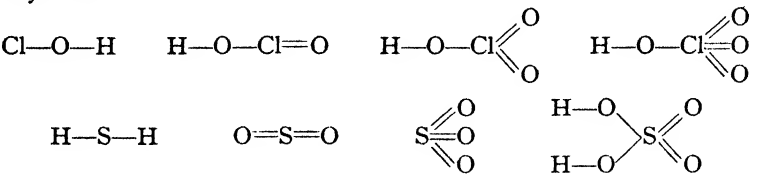
An important step in chemical theory was taken in 1852 by Frankland in the statement of the *Theory of Valency*. He supposed that atoms have units of combining capacity, which they saturate in combination with one another, and represented these so-called valencies by bonds drawn from the atom symbols :

Frankland supposed that the valency of an atom could vary in different types of compounds, but Kekulé assumed that the valency was fixed, which necessi-

tated some artificial formulae ; iron, for example, retained a valency of three when the ferrous compounds were supposed to be polymerised :



Blomstrand, a follower of Berzelius, in 1869 gave formulae in which elements such as chlorine, nitrogen, and sulphur have different valencies in their oxides and oxy-acids :



The theory of *Electrolytic Dissociation* proposed by Arrhenius in 1887 indicated that ions have different valencies according to their electrical charges (p. 101), the ferrous and ferric ions, for example, being Fe^{++} and Fe^{+++}, with different chemical properties. It was obvious that the valency of an ion is identical with its charge. In the same way, it seemed as if the formula of an uncharged compound could be represented by balancing the positive and negative valencies attributed to the atoms, although in many cases these charged atoms were not known as independent ions :

H and alkali metals +1.	S,Se,Te −2, +4 and +6.
Alkaline earth metals, Zn,Cd,Hg +2.	Cr +2, +3 and +6.
B,Al, rare earths +3.	F −1.
Ga,In,Tl +1 and +3.	Cl,Br,I −1, +3, +5 and +7.
Si +4.	Mn +2, +3, +4, +6 and +7.
Ge,Sn,Pb +2 and +4.	Fe,Co,Ni +2, +3 and +6.
N +3.	Platinum metals, various values from +1 to +8.
P,As,Sb,Bi +3 and +5.	
O −2.	

S −2 in H_2S and sulphides ; +4 in SO_2, sulphites and derived compounds such as $SOCl_2$; +6 in SO_3, sulphates and derived compounds.

Cl −1 in HCl and chlorides of metals ; +3 in chlorous acid $HClO_2$ and related compounds ; +6 in chloric acid $HClO_3$ and related compounds ; +7 in perchloric acid $HClO_4$ and related compounds.

In oxygen compounds the valency of the other element is always positive, oxygen being always negative, as in Berzelius's system.

In this way, quite complicated formulae may readily be checked.* Thus, the following satisfy the rules :

$K_2Cr_4O_{13}$ (2 + 24 − 26)	$Na_2[MoO_2F_4]$ (2 + 6 − 4 − 4)
$(NH_4)_6Mo_7O_{24}$ (6 + 42 − 48)	$H_{10}W_{12}O_{41}$ (10 + 72 − 82)
$H_3[PMo_{12}O_{40}]$ (3 + 5 + 72 − 80)	$Ba_5(IO_6)_2$ (10 + 14 − 24).

* McAlpine and Soul, *Qualitative Chemical Analysis*, 1933, 629.

In many cases the valency of a radical can be used instead of resolving the formula into atoms :

$$MnAl_2(SO_4)_4 \ (2+6-8) \qquad K_4[Mn(CN)_6] \ (4+2-6)$$

The formulae of compounds of the platinum metals in the table on p. 878 provide a good example of the rules.

Carbon, an element with practically no electrochemical character, does not fit into this scheme, and it cannot be applied to inorganic compounds in which atoms are linked in chains, as in the peroxides containing the group —O—O—.

In *Werner's Theory* (1893) the elementary view of valency was extended (p. 213) to such compounds as K_2PtCl_6, which could not be formulated with the valencies 1, 4 and 1 for K, Pt, and Cl ; the ion $[PtCl_6]''$ was formulated as a *nucleus* in which six atoms of chlorine are linked to an atom of 4-valent platinum to give a valency of $+4-6=-2$, in accordance with the above rules, and the "central atom," Pt, is *coordinated* with six atoms; in $[Fe(CN)_6]''''$ $(+2-6=-4)$ there are six radicals ; in $[Co(NH_3)_6]'''$ six neutral molecules. The *co-ordination number* six applies to a great number of compounds, and the tendency for it to appear quite overweighs the operation of the normal valencies. Other coordination numbers are 4 and 8.

The discovery of the negative electron in 1897 changed very little in Chemistry ; its existence has been postulated since Faraday's time, and practically everything was known about it except its mass. It had been invoked by Helmholtz in 1881 to explain valency, and *electronic theories of valency* flourished later in various forms. The first significant theories of this kind were those proposed by Kossel in 1916 to explain *electrovalency*, and in the same year by G. N. Lewis to explain *covalency* (of the type met with in carbon compounds) ; the combination of the two theories gave a successful explanation of Werner's theory.

In Kossel's theory emphasis was laid on a tendency for the *transfer* of electrons from one atom to another, so as to produce charged ions having stable outer shells of electrons (represented by dots in the symbols below) ; usually groups of eight (octets), which form the outer shells of the very stable inert gas atoms. In Lewis's theory, the formation of a stable outer group of electrons on each atom is achieved in covalent (unitary) compounds by the *sharing* of electrons by the outer shells of two atoms, each shared pair of electrons constituting an ordinary single valency bond. In some cases, this pair of electrons is contributed by one atom ; the resulting link, having some ionic and some covalent character, has received various names (*e.g.* semi-polar double bond, or dative bond, coordinate or co-ionic link, etc.) :

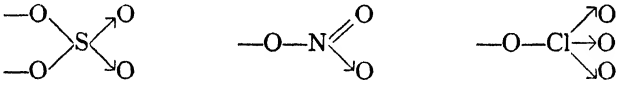
$$A\cdot + \cdot\dot{\underset{\cdot\cdot}{\overset{\cdot\cdot}{B}}}: = A^+ + [:\dot{\underset{\cdot\cdot}{\overset{\cdot\cdot}{B}}}:]^- \quad \text{ionic link}$$

$$:\dot{\underset{\cdot\cdot}{\overset{\cdot\cdot}{A}}}\cdot + .\dot{\underset{\cdot\cdot}{\overset{\cdot\cdot}{B}}}: =: \dot{\underset{\cdot\cdot}{\overset{\cdot\cdot}{A}}}: \dot{\underset{\cdot\cdot}{\overset{\cdot\cdot}{B}}}: \text{ or } A—B \quad \text{covalent link}$$

$$A: + \dot{\underset{\cdot\cdot}{\overset{\cdot\cdot}{B}}}: = A: \dot{\underset{\cdot\cdot}{\overset{\cdot\cdot}{B}}}: \text{ or } A\rightarrow B \quad \text{coordinate link}$$

The enunciation of the *Quantum Theory* by Planck in 1900 produced much more far-reaching effects than the discovery of the electron. Previously, it was generally thought that Dynamics, based on Newton's laws of motion, was the fundamental science, and that others should ultimately be reduced to applications of it. The kinetic theory of gases had shown that heat may be regarded as the kinetic energy of moving molecules, and it was believed that all energy should be explained in terms of moving matter: even when no matter is present, as in electromagnetic waves in a vacuum, it was thought necessary to introduce a hypothetical matter, the ether, with properties more bizarre than those of phlogiston; some enthusiasts even proposed that ordinary matter should be explained in terms of ether. The quantum theory cut across such dynamical theories and was incompatible with them; it envisaged transfers of energy in discrete quanta rather than continuously, and it drastically changed the whole of Physics. It entered into Bohr's theory of the atom, the first to have any physical validity, and so it spread into Chemistry, extending and deepening the conception of valency (p. 255).

The *theory of resonance*, a product of modern quantum theory, has reacted very profoundly on the electronic formulation of bond types, and the present position is very different from that of about 1930, when the formulae of the anions of oxy-acids, for example, contained coordinate links, in order to preserve the supposed octet of electrons around each atom, rather than the older double bonds. In the case of nitric acid, three different bonds were supposed to unite the three atoms of oxygen to the nitrogen:



The theory of resonance, whose findings are supported by measurements of bond distances and energies, supposes that the actual electronic configuration in such cases is one which gives equivalent bonds, in some cases approaching single- and in others double-bond character, and the state of an ion or molecule sometimes cannot be represented by any single chemical formula. Very crudely put, it is as though, if one *electronic* arrangement (the atomic nuclei are supposed to remain in one configuration) would appear blue and another red, the actual state would not be a mixture of red and blue molecules (which would correspond with tautomerism), but one in which all the molecules have some uniform shade of purple. The formulation of inorganic compounds is thus much less simple than was once assumed.

Limitation of space prevented a discussion in the book of alternative theories of bond formation, and the method of Heitler and London was deliberately chosen as being in closer contact with chemical views than the method of " molecular orbitals " of Mulliken, although the latter method has its advantages. The student will find both methods more fully described in the references given.

In Chapter X an attempt is made to indicate the way in which the quantum theory enters not only the theory of valency but also the structure of the Periodic

Table. The quantum theory, like some other fundamental principles, has a negative character: it assumes that, out of the continuum of atomic energy states permitted by Newtonian dynamics, only a finite number have actual existence, all intermediate states having no reality. This introduces the concept of *quantum numbers*, by which the permitted states are defined. It is noteworthy that, in basing the explanations of valency and of the Periodic Table on quantum conceptions, an empirical principle, which at present has no theoretical foundation, has to be assumed, viz. Pauli's principle, that no two electrons in an atom can have the same set of quantum numbers. The explanation of this, and of other things as yet unsolved, remains for the future. We may be sure that this holds many treasures, and not a few surprises, in reserve.

PART I

GENERAL AND PHYSICAL CHEMISTRY

CHAPTER I

ATOMIC AND MOLECULAR WEIGHTS

Elements and Compounds

Homogeneous and heterogeneous bodies.—Different kinds of bodies have different properties when examined in bulk under identical conditions. Some are **homogeneous** or of the same kind throughout, whilst others are **heterogeneous** or of different kinds in different parts (" mechanical mixtures "). The different parts of a heterogeneous body are called **phases.** A mixture of ice and water consists of two phases, whilst a homogeneous body, even if divided into several parts in space (*e.g.* separate pieces of ice floating in water), forms only one phase (ice).

When the molecular structure is taken into account the meaning of homogeneity requires further consideration. We can effectively avoid such difficulties by restricting homogeneity to a lower limit of size of optical differentiation (microscopic or, to include colloidal solutions as heterogeneous, ultramicroscopic, examination), *i.e.* to volumes of the order of $(5 \times 10^{-5}$ cm.$)^3$. This is not the lowest experimentally attainable limit, but is the effective limit for the definitions given here. A true solution is here regarded as homogeneous, whereas if single molecules could be seen it would be heterogeneous.

The law of conservation of mass.—The **mass** of a body is measured by comparison with standards with an ordinary balance, and the **law of conservation of mass** (clearly stated by Lavoisier but recognised before his time) asserts that *the total mass of a system is constant*, even though it undergoes chemical change.

This was shown to be exact by Landolt's experiments, begun in 1893 and completed in 1908. He sealed up in separate legs of a Jena glass U-tube (Fig. 1) solutions of substances which react without much evolution of heat, *e.g.* hydriodic acid and iodic acid, giving a precipitate of iodine, and chloral hydrate and caustic potash, giving an emulsion of chloroform. The tube was counterpoised against an exactly similar filled tube on a balance detecting a change of weight of 0·0001 g. with a load of 1 kg. in each pan, *i.e.* a change of 1 part in 10,000,000. One tube was inverted, and after cooling replaced on the balance and the change in weight noted.

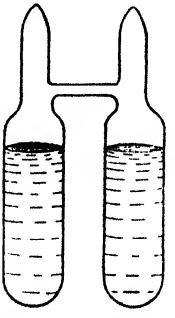


Fig. 1.—Landolt's experiment.

Slight diminutions in weight, 0·167 mg. in the maximum, were found, but these were traced to two causes, both the result of the slight evolution of heat: (*a*) the film of moisture on the outer surface of the glass was partly driven off and did not return until after long standing; (*b*) the vessel expanded slightly, and did not recover its original volume for some time.

The first effect reduced the weight of the vessel, and the second, which increased the volume of air displaced by the vessel, reduced the apparent weight. By allowing the vessel to stand for a long time before reweighing, Landolt found that it recovered its original weight to 1 part in 10,000,000—*i.e.* within the limits of experimental error. By using silica tubes (which do not expand) covered with wax (to prevent the formation of a film of moisture), no change in weight was found within the same limits of error. Experiments by Manley (1912) reduced the limit of error to 1 in 100,000,000 for the reaction between barium chloride and sodium sulphate. The law of conservation of mass may thus be considered to be exact.

According to the Theory of Relativity, the absolute energy E of a mass m is $E = mc^2$, where c is the velocity of light. A chemical change attended by a loss of energy ΔE will give rise to a loss of mass $\Delta m = \Delta E/c^2$. Since c is very large this will be quite negligible in ordinary reactions. A loss of only 1 mg. should occur in the combustion of $3\frac{3}{4}$ tons of phosphorus. In radioactive changes the loss of mass should be larger (p. 208).

Elements and compounds.—Homogeneous bodies may either have a constant composition, however prepared, when they are called **pure substances**, or they can be prepared with different compositions, when they are called **solutions**. Solutions can always be separated by suitable means (*e.g.* evaporation or distillation) into two or more pure substances.

A homogeneous pure substance may undergo chemical change in different ways according to its composition :

(i) It forms products of greater weight than itself in all changes, or *combines* with other substances, when it is called an **element**.

(ii) It forms products each of less weight than itself, or *decomposes*, when it is called a **compound**.

(iii) It remains unchanged in weight, when it is said to have undergone an **allotropic change** if it is an element, or an **isomeric change** if it is a compound.

Sometimes a change in physical state of a *compound, e.g.* red into yellow mercuric iodide on heating, is called an allotropic change. A few elements, such as argon, do not undergo chemical changes.

The separation of a compound into its elements is called **analysis** ; the formation of a compound from elements is called **synthesis**, although both these terms are also used with different meanings.

Many elements are mixtures of two or more varieties called **isotopes** (p. 185), but when these are present in constant ratios and are inseparable by ordinary chemical changes the particular mixture behaves as a simple element.

Occurrence of the elements.—There are about ninety elements, of which about thirty are sometimes found in the free state. At atmospheric temperature eleven are gases, two liquids, and the rest solids with melting points varying from 28° to about 3000°. About two-thirds of the terrestrial elements have been spectroscopically detected in the atmosphere of the sun, and no new elements are present in the sun, stars or nebulae. About a dozen elements compose 93 p.c. of terrestrial matter. An estimate of the occurrence of the

were suspended one on each arm of the balance when the *exhausted* density globe was weighed.

The globe method has been improved by Moles, who claims an accuracy of 1 in 10^5. He introduced the following refinements :

(1) The globe was surrounded by melting ice, the temperature of which was checked by a Beckmann thermometer.

(2) Rubber connections carrying mercury were dispensed with.

(3) The mercury in the manometer and gas leading tubes was kept at a constant temperature by water circulating through a thermostat or by immersion in ice.

(4) Mercury never came in contact with tap grease.

(5) Only pure dry air entered the lower manometer chamber, and the gas pressure in the density bulbs was equalised through a gauge containing " apiezon " oil of negligible vapour pressure.

(6) Oil or mercury fog was prevented from entering the bulbs by fritted glass filters.

(7) Adsorption was measured for each gas on glass of the same composition as the bulb and a correction appropriate to the filling pressure was applied.

(ii) **The volumeter method.** In this a known weight of gas is admitted to a vacuous vessel of known volume and the resulting pressure is measured, or a gas in a vessel of known volume at a known pressure is condensed in a *small* vessel in which it is weighed. In this method the assumption that the gas obeys Boyle's law is sometimes necessary.

Morley used this method to determine the *density of hydrogen*. Very pure dry electrolytic hydrogen was brought in contact with metallic palladium heated in an exhausted glass tube and the metal allowed to cool in the gas. A large volume of hydrogen was taken up and the unabsorbed gaseous impurities were pumped out of the tube. On heating the palladium to dull redness pure hydrogen was evolved, and was received in three large exhausted glass globes of accurately known total volume, immersed in ice. The rise in pressure in the globes was measured by a mercury manometer. The weight of hydrogen was found from the loss in weight of the tube containing the palladium.

One of Morley's results is given below :

Volume of the three globes - - -	43·2574 lit.
,, ,, gas space in manometer -	0·0550 ,,
,, ,, connecting tubes - -	0·0365 ,,
Total volume of gas - - - -	43·3489 ,,

Temperature, 0°. Pressure, 725·40 mm. Loss of weight of palladium bulb = weight of hydrogen = 3·7164 g.

Correction factor to reduce weighings to sea-level and 45° latitude and length of cathetometer to 0° = 1·00044.

$$\therefore \text{ normal density of hydrogen} = \frac{3{\cdot}7164}{43{\cdot}3489} \times \frac{760}{725{\cdot}4} \times 1{\cdot}00044 = 0{\cdot}089861 \text{ g./lit.}$$

As a mean result Morley found:

normal density of hydrogen = 0·089873 ± 0·0000027 g./lit.,
normal density of oxygen = 1·42900 ± 0·000034 g./lit.

Morley's value for hydrogen when referred to the latitude of Paris is 0·089901, differing from Regnault's value 0·08988 by less than 1 part in 4000.

The *density of hydrogen chloride* was determined by Gray and Burt (*J.C.S.*, 1909, **95**, 1633) with the apparatus shown diagrammatically in Fig. 3. The gas was collected in the bulb *A* of accurately known volume (*c.* 450 c.c.), which was rigorously dried by evacuating, heating, filling with dry air and exhausting repeatedly. This was kept at 0° and the gas collected at atmospheric pressure, the excess bubbling through sulphuric acid in *h*. The pressure was read on a standard barometer. The air in the capillaries and in the weighed bulb *B* (*c.* 20 c.c.) containing gas-free charcoal was removed by immersing another charcoal bulb *C* in liquid air, the tap *a* being closed. The tap *c* was closed and *a* opened, and the bulb *B* immersed in liquid air. All the gas from *A* condensed on the charcoal in *B*, which was then shut off, detached at the ground joint, and weighed against a compensating bulb. The bulb *A* could be refilled with gas and the process repeated. No shrinkage correction was necessary for the small bulb *B*, but a correction was necessary for the hydrogen chloride adsorbed on the walls of the glass bulb *A*, which passed into *B* when *A* became vacuous; this adsorbed gas amounted to 0·1235 cu. mm. per sq. cm. A silica bulb *A* was also used, which was easier to dry and no correction for adsorption was then necessary. A small correction was applied for the deviation from Boyle's law in reducing atmospheric pressure to 760 mm., and also a correction in reducing the barometric pressure from the latitude of London to latitude 45°. The average normal density of HCl from three series of measurements was 1·63915 g./lit.

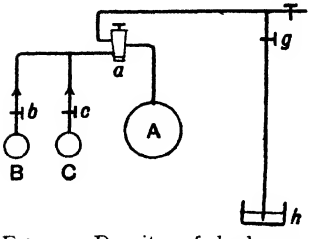


FIG. 3.—Density of hydrogen chloride by volumeter method.

(iii) **The microbalance method.** This method is now mostly used to find the *limiting density* (density at S.T.P. reduced to the ideal state), and is described further on, after a discussion of limiting densities.

The following are the accurate normal densities of some important gases (see *Ann. Rep. C.S.*, 1938, 131):

Hydrogen	0·08987	Oxygen	1·42900
Methane	0·7168	Hydrogen sulphide	1·5384
Ammonia	0·7714	Hydrogen chloride	1·6392
Carbon monoxide	1·2502	Argon	1·7836
Nitrogen	1·25046	Carbon dioxide	1·9769
Ethylene	1·26036	Nitrous oxide	1·9777
Air (dry, CO_2 free)	1·2927	Sulphur dioxide	2·9266
Nitric oxide	1·3402	Chlorine	3·214

Limiting densities.—Since actual gases deviate somewhat from Boyle's law, the density at S.T.P. gives only an approximate molecular weight. At very low pressures, however, experiments show that gases obey Boyle's law strictly, and hence Avogadro's hypothesis then becomes exact.

If a mass W g. of gas occupies a volume V lit. at 0° under a pressure p atm., W/pV is the *density* (W/V) *at unit pressure*. Owing to deviations from Boyle's law pV is not quite constant at different pressures. When $p = p_1 = 1$ atm. the quotient is the *normal density* $D = W/p_1V_1$, where $p_1 = 1$. As p approaches zero pV tends to the value p_0V_0 and the quotient W/pV approaches the value for the ideal gas, and is called the *limiting density* D_0:

$$D_0 = W/p_0V_0.$$

Hence:
$$D_0 = D \times (p_1V_1/p_0V_0). \quad \ldots\ldots(1)$$

D_0 is the weight *at S.T.P.* of 1 lit. of the gas in the ideal state, and by dividing the molecular weight M by this, the molar volume of the ideal gas at S.T.P. is found. For oxygen $(M = 32{\cdot}0000)$ this is found from the limiting density D_0 to be 22·415 lit., and since this is the same for all gases in the ideal state, by Avogadro's hypothesis, we have for *any* gas:

$$M = 22{\cdot}415D_0, \quad \ldots\ldots(2)$$

where D_0 is its limiting density as defined by (1).

By plotting pV against p a straight line is found for most gases for values of p less than 1 atm., and hence by extrapolation the value of p_0V_0 for $p = 0$ is found. This is the value corresponding with Boyle's law (Rayleigh, 1902).

The linear relation between pV and p holds only for permanent gases; for more easily liquefiable gases the $pV - p$ isothermals are probably slightly curved, the slope decreasing somewhat at lower pressures, but the curvature is quite small even for carbon dioxide. The accurate equation is

$$pV = p_0V_0 + Bp + Cp^2 + \text{etc.},$$

but C is very small and the term is negligible at pressures below atmospheric.

D. Berthelot (1904) defined the *compressibility coefficient* between 1 atm. (p_1) and zero pressure (p_0) as:

$$A_0^1 = \frac{p_0V_0 - p_1V_1}{p_0V_0(p_1 - p_0)}. \quad \ldots\ldots(3)$$

From (1) and (3) we find (with $p_1 = 1$, $p_0 = 0$):

$$D_0 = D(1 - A_0^1). \quad \ldots\ldots(4)$$

A different compressibility coefficient was used by Guye (1913), viz.

$$\lambda = \frac{p_0V_0 - p_1V_1}{p_1V_1(p_1 - p_0)}; \quad \ldots\ldots(5)$$

$$\therefore\ D_0 = \frac{D}{1 + \lambda}. \quad \ldots\ldots(6)$$

The values of A_0^1 are usually positive, those of λ negative, and the two definitions are not identical (Cawood and Patterson, *J.C.S.*, 1933, 619; Dietrichson, Orleman and Rubin, *J.A.C.S.*, 1933, **55**, 14).

The limiting density method for the determination of molecular weights, introduced by D. Berthelot in 1899, has been used by Guye, R. Whytlaw-Gray, and Moles, and their pupils. Moles finds that if allowance is made for adsorption on the glass globe the *density* (weight of 1 lit. at S.T.P.) of any gas is a linear function of pressure below 1 atm.:

$$D = D_0 + ap.$$

(This is a different relation from $pV = p_0V_0 + Bp$.)

Example 1.—Gray and Burt's results for hydrogen chloride were:

Normal density $D_1 = 1{\cdot}63915$ g./lit. (corrected for adsorption).

$p_1V_1 = 54803$, $p_0V_0 = 55213$ (by graphical extrapolation, as the pV–p graph showed a slight curvature).

$$\therefore \text{ limiting density} = D_0 = D \times (p_1V_1/p_0V_0)$$
$$= 1{\cdot}63915 \times 54803/55213 = 1{\cdot}62698 \text{ g./lit.}$$

The normal density of hydrogen is 0·089873 (Morley) and $\lambda = -0{\cdot}00054$, hence the limiting density is:

$$D_{0\,H_2} = 0{\cdot}089873/(1 - 0{\cdot}00054) = 0{\cdot}089922 \text{ g./lit.}$$

The molecular weight of HCl (H = 1) is thus $2 \times 1{\cdot}62698/0{\cdot}089922 = 36{\cdot}186$, and the atomic weight of chlorine (H = 1) is 35·186.

Example 2.—The densities at unit pressure (W/pV) of nitrous oxide at different pressures (p atm.) and the values of pV found by Batuecas (1931) were:

p	1·00	0·667	0·50	0·333
W/pV	1·9804	1·9746	1·9722	1·9694
pV	1·00000	1·00294	1·00416	1·00559

Extrapolation of the pV–p curve gave p_0V_0, and $1 + \lambda = 1{\cdot}0085$.

$$\therefore D_0 = D_1/(1+\lambda) = 1{\cdot}9804/1{\cdot}0085 = 1{\cdot}9637 \text{ g./lit.}$$
$$\therefore M = 1{\cdot}9637 \times 22{\cdot}415 = 44{\cdot}016.$$
$$\therefore \text{ at. wt. } N = \tfrac{1}{2}(44{\cdot}016 - 16) = 14{\cdot}008.$$

Another method of finding the limiting density is to use an equation which corrects the deviations from the ideal gas laws, *e.g.* van der Waals's equation (p. 35) or the more accurate Berthelot's equation (p. 13). This corrects the so-called general gas law, derived in the next paragraph.

The general gas law.—The behaviour of gases towards changes of pressure and temperature are approximately represented by Boyle's law and Charles's law.

Boyle's law (1662) states that *the volume of a fixed mass of gas at constant temperature is inversely proportional to the pressure*:

$$V_1/V_2 = p_2/p_1, \quad \therefore p_1V_1 = p_2V_2 \text{ or } pV = \text{const.} \quad \ldots\ldots\ldots\ldots(1)$$

Charles's law (1787) states that *the volume of a fixed mass of gas at constant pressure increases by* $\frac{1}{273}$ *of the volume at* 0° C. *for each* 1° C. *rise in temperature.*

If V_0 and V_t are the volumes at 0° C. and t° C.,

$$V_t = V_0 + V_0 \cdot \frac{t}{273} = V_0\left(1 + \frac{t}{273}\right) = V_0 \frac{t+273}{273}.$$

For two temperatures t_1 and t_2,

$$V_2/V_1 = (t_2+273)/(t_1+273) = T_2/T_1, \quad \ldots\ldots(2)$$

where $T = t° \text{ C.} + 273$ (more accurately 273·09) is the *absolute temperature*; hence *at constant pressure the volume is proportional to the absolute temperature.* It is easily shown from (1) and (2) that *at constant volume the pressure is proportional to the absolute temperature.*

When both pressure and temperature change, let p_1, V_1, T_1 and p_2, V_2, T_2 be corresponding pressures, volumes, and absolute temperatures. If p_1 is changed to p_2 whilst T_1 is constant, the volume becomes $V_1 \cdot p_1/p_2$ by (1). If T_1 is now changed to T_2 whilst p_2 is constant, the volume changes to $V_1 \cdot \frac{p_1}{p_2} \cdot \frac{T_2}{T_1}$ by (2), and this must be V_2.

$$\therefore \quad V_1 \frac{p_1}{p_2} \cdot \frac{T_2}{T_1} = V_2 \quad \text{or} \quad p_1 V_1/T_1 = p_2 V_2/T_2;$$

$$\therefore \quad pV/T = \text{const.} \quad \ldots\ldots(3)$$

Avogadro's hypothesis shows that if the mass of gas at S.T.P. is 1 mol (1 g. mol. wt.), V is the same (22·415 lit.) for all gases. Let the constant in (3) per mol be denoted by $\mathbf{R}$, the *general gas constant.* Then at S.T.P.

$$pV/T = \mathbf{R} = 1 \times 22{\cdot}415/273{\cdot}09 = 0{\cdot}08208 \text{ lit. atm./degree C.}$$

and

$$pV = \mathbf{R}T. \quad \ldots\ldots(4)$$

It should be noted that V in (4) is the volume of 1 mol of gas. If n mols of gas occupy a volume V lit., the volume of 1 mol is V/n lit., and (4) becomes

$$p(V/n) = \mathbf{R}T; \quad \therefore \; pV = n\mathbf{R}T. \quad \ldots\ldots(5)$$

Care should be taken to use the correct value of $\mathbf{R}$ in different problems, since it can be expressed in various units; in calculations of gaseous volumes the value given above should be used.

Berthelot's equation.—D. Berthelot modified the ideal gas equation:

$$pV = \mathbf{R}T \quad \ldots\ldots(1)$$

by allowing for (i) the finite volume of the molecules and (ii) the attractive forces between them in an actual gas (see p. 35), and so obtained the equation:

$$pV = \mathbf{R}T\left[1 + \frac{9T_c(T^2 - 6T_c^2)}{128 p_c T^3} p\right], \quad \ldots\ldots(2)$$

where p_c = critical pressure, and T_c = absolute critical temperature. If V is in

lit. and p and p_c in atm., $\mathbf{R}$ is 0·08208 lit. atm./1° C. Since $V = M/D$, where M = mol. wt. and D = normal density, and the expression in square brackets may be written as $(1 - Ap)$, (2) may be written :

$$M = \frac{D\mathbf{R}T}{p}(1 - Ap), \quad \text{.....(3)}$$

where

$$A = -\frac{9}{128}\frac{T_c}{p_c}\frac{(T^2 - 6T_c^2)}{T^3}. \quad \text{.....(4)}$$

For hydrogen chloride $D = 1{\cdot}63915$, $t_c = 51{\cdot}45°$ C., $p_c = 81{\cdot}55$ atm. Thus $A = +0{\cdot}007658$ and $M = 1{\cdot}63915 \times 0{\cdot}08208 \times 273{\cdot}09 \times 0{\cdot}992342 = 36{\cdot}460$, and the atomic weight of chlorine = 36·460 − 1·008 = 35·452. The accepted value is 35·457, so that Berthelot's equation gives a very good result.

The microbalance.—Some very accurate determinations of molecular weights of gases have been made with the microbalance, invented by Nernst, and used by R. W. Gray and Ramsay in 1910 for the determination of the density of radium emanation (in which a balance with a sensibility of 1/500,000 mg., dealing with a volume of 0·1 cu. mm., weighing less than 0·001 mg., was used). It has since been improved (Cawood and Patterson, *Phil. Trans.*, 1936, **236**, 77 ; Roberts, Emeléus and Briscoe, *J.C.S.*, 1939, 41), and a modern form is shown diagrammatically in Fig. 4. The beam, suspension fibres and parts of the frame were of fused quartz, the bulbs and most of the frame (shown thickened) of pyrex glass. The beam was 50 mm. × 1 mm., the bulbs were 19·4 and 13·7 mm. diameter with outer surfaces in the ratio $\sqrt{2} : 1$, and since the smaller bulb was pierced on the axis of the beam, both had the same exposed surface. A cross-bar of very light quartz rod sealed on at the " centre of surface " was also at the centre of gravity. The bent pointer was attached to the buoyancy bulb A and the reading microscope was end-on. The whole was enclosed in a glass cylinder 130 mm. × 25 mm., containing the gas, with a plate-glass window at one end and a capillary connection to the pressure system. The adjustment in air was at rather less than 1 atm. pressure and the period of oscillation was 10 sec. Pressure differences of 0·005 mm. were indicated.

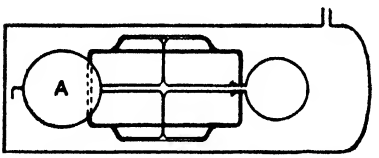


FIG. 4.—Microbalance (plan).

The beam is balanced at zero when the gas density in the case exerts a buoyancy effect on the bulb which compensates its net weight. The pressures p_I and p_{II} at which two gases have equal densities are measured.

From (3), p. 11, ($p_0 \to 0$, $p_1 = p$) :

$$pV = p_0V_0(1 - A_0^1 p).$$

But $p_0V_0 = (W/M)\mathbf{R}T$ for an ideal gas, and $W/V = D$, the normal density ;

$$\therefore\ p = \mathbf{R}TD(1 - A_0^1 p)/M.$$

Hence for equal densities :

$$\frac{p_{\mathrm{I}}}{p_{\mathrm{II}}} = r = \frac{M_{\mathrm{II}}(1 - A^1_{0\,\mathrm{I}} p_{\mathrm{I}})}{M_{\mathrm{I}}(1 - A^1_{0\,\mathrm{II}} p_{\mathrm{II}})};$$

$$\therefore \frac{M_{\mathrm{II}}}{M_{\mathrm{I}}} = r \cdot \frac{(1 - A^1_{0\,\mathrm{II}} p_{\mathrm{II}})}{(1 - A^1_{0\,\mathrm{I}} p_{\mathrm{I}})}.$$

The balancing pressure ratio r may be extrapolated to the limiting value r_0 for $p_{\mathrm{I}} = p_{\mathrm{II}} = 0$.

$$\therefore \frac{M_{\mathrm{II}}}{M_{\mathrm{I}}} = r_0.$$

If the compressibility coefficient $A^1_{0\,\mathrm{I}}$ of one gas is known, that of the other gas may be calculated from the values of r at two pressures below 1 atm. :

$$\frac{r'}{r''} \times \frac{1 - p'_{\mathrm{II}} A^1_{0\,\mathrm{II}}}{1 - p''_{\mathrm{II}} A^1_{0\,\mathrm{II}}} = \frac{1 - p'_{\mathrm{I}} A^1_{0\,\mathrm{I}}}{1 - p''_{\mathrm{I}} A^1_{0\,\mathrm{I}}}.$$

This microbalance method has been used, *e.g.* to determine the atomic weight of carbon (see p. 476) from the density of carbon monoxide (Woodhead and R. Whytlaw-Gray, *J.C.S.*, 1933, 846). Corrections were applied for the shrinkage of the buoyancy bulb caused by change of gas pressure outside, and for the shift in the centre of gravity of the bulb due to this shrinkage.

Series	Approx. pressures, mm.		Uncorrected ratio	Corrections	Corrected ratio
	O_2	CO			
I. 0° C.	382·8	437·2	0·87526	− 0·00010	0·87516
II. 19·8° C.	181·9	207·8	$0{\cdot}87535_5$	− 0·000123	0·87523
III. 19·8° C.	361·9	413·5	$0{\cdot}87524_7$	− 0·000112	0·87514
IV. 19·8° C.	572·3	654·0	$0{\cdot}87509_8$	− 0·000099	0·87500

The value from series I was rejected as being less accurate. Three values from series II, III and IV for the limiting ratio at zero pressure were found by plotting the ratio against the pressure and extrapolating to zero pressure. By multiplying the ratio at zero pressure by 32·000 (the molecular weight of normal oxygen) the molecular weight of carbon monoxide is found.

	Limiting ratio, $p = 0$	Mol. wt. of carbon monoxide
Series II and III	0·87533	28·010(6)
Series II and IV	0·87534	28·011(0)
Series III and IV	0·87537	28·011(8)

Taking the value 28·011, the atomic weight of carbon is found to be

$$28{\cdot}011 - 16{\cdot}000 = 12{\cdot}011.$$

Although the value 12·00 was long in use, the detection of the isotope of carbon of mass 13 showed that it should be raised to about 12·01, and this is confirmed by the above measurements.

The microbalance method has several advantages over the globe method (p. 8) for the determination of gas densities; *e.g.* (1) it requires a smaller

quantity of gas, which is thus more easily procured in a state of great dryness and purity, and (2) it minimises errors due to (*a*) buoyancy corrections, (*b*) shrinkage, (*c*) adsorption of moisture on the outside of the globe, and (*d*) adsorption of gas on the inside of the globe.

Vapour Density

Since vapours obey the gas laws approximately, the **vapour density** may be found if the weight of any volume of the vapour measured under the actual temperature and pressure of the experiment is known.*

The weight of V c.c. (or ml.) at a temperature $t°$ and under a pressure of P mm. of a vapour of normal density D is :

$$V \times \frac{D}{1000} \times \frac{273}{273+t} \times \frac{P}{760} \text{ g.}$$

The vapour density may be determined by three methods ; that selected depends on the conditions of experiment, *e.g.* whether a high or low temperature, or pressure, is used.

Hofmann's method.—In this (A. W. Hofmann, 1868) the volume of a given weight of vapour is found. A wide barometer tube, about 1 m. long and carefully graduated in ml., is surrounded with a glass jacket through which the vapour of a liquid boiling in a separate vessel is passed. The vapour jacket is provided with a tube at the bottom for leading the vapour to a condenser (Fig. 5). Uniformity of temperature is thus assured.

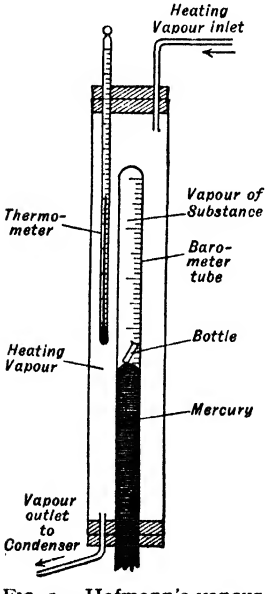


Fig. 5.—Hofmann's vapour density apparatus.

The liquid is weighed in a small bulb with a ground stopper, which is forced out when the bulb is passed into the vacuous space of the upper part of the barometer tube, and the liquid volatilises. The bulb must be completely filled with liquid, since a bubble of air will expand considerably in the vacuous space.

Since volatilisation occurs under reduced pressure, steam may be used in the jacket for liquids boiling up to 180° at atm. pressure. If the atm. pressure differs from 760 mm. the b.p. of the liquid must be corrected, or a thermometer hung in the jacket.

When the mercury level in the heated barometer tube is constant, the following data are noted :

(i) The volume of the vapour = V ml.

(ii) The temperature $t°$ in the jacket.

(iii) The pressure of the vapour, approximately the barometric height H mm. *minus* the height of mercury in the tube above the level in the trough h mm., *i.e.* $(H - h)$ mm.

* The name *vapour density* was formerly used for the ratio of the weight of any volume of the vapour of a substance to the weight of an equal volume of hydrogen at the same temperature and pressure (p. 8).

In accurate work, the height of the *heated* mercury must be reduced to 0°, to correspond with the corrected barometer, and allowance made for the expansion of the scale of the glass tube. The vapour pressure of mercury at the temperature of the jacket is also subtracted from the pressure of the vapour at higher temperatures.

Then the known weight of substance taken is given by :

$$m = V \times \frac{D}{1000} \times \frac{273}{273+t} \times \frac{H-h}{760} \text{ g.},$$

from which D may be calculated.

EXAMPLE.—0·338 g. of carbon tetrachloride gave 109·8 c.c. of vapour at 99·5°. Barometric height = 746·9 mm. Height of mercury in tube above level in trough = 283·4 mm.

$$\therefore\ 0{\cdot}338 = 109{\cdot}8 \times \frac{D}{1000} \times \frac{273}{372{\cdot}5} \times \frac{463{\cdot}5}{760}.$$

$$\therefore\ D = 6{\cdot}884 \text{ g./lit.} \quad \text{The molecular weight is } 22{\cdot}4D = 154{\cdot}2.$$

Dumas' method.—In this method (Dumas, 1826) the weight of a given volume of vapour is determined. Since the vapour does not come in contact with mercury, the method may be used for substances (*e.g.* bromine) which cannot be dealt with by Hofmann's method. It is not so accurate as this, and as the temperature of the vapour is higher under atmospheric pressure, it cannot be used for substances which readily decompose.

A thin glass bulb (Fig. 6) of about 200 c.c. capacity with a drawn-out neck is cleaned, dried, and weighed. By warming the bulb, dipping the neck in the liquid, and cooling, enough liquid is drawn into the bulb to expel all the air when it is vaporised.

The bulb is weighed again and is then quickly immersed in a water-bath (or melted paraffin wax, 30°–40° above the boiling point of the liquid), so that the tip projects above the surface of the liquid. The bulb is conveniently held in a wire spring clip with a wooden handle, as shown. Volatilisation occurs rapidly, the air being expelled. When the rush of vapour ceases the neck of the globe is sealed off, and the temperature of the bath is read.

The globe is removed, cooled, cleaned, and weighed along with the piece of neck sealed off. The neck is then scratched with a file and the tip broken off under previously boiled water, which rushes into the bulb and, if the experiment has been successful, fills it completely. The bulb full of water is weighed on a rough balance to 0·1 g. The barometric pressures are noted.

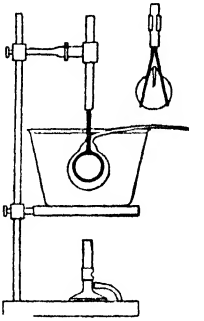


FIG. 6.—Dumas' vapour density apparatus.

Reproduced from Palmer's Experimental Physical Chemistry (C.U.P.)

The weight of vapour may sometimes be found by chemical methods. *E.g.* if iodine has been used, the tip of the bulb is broken under potassium iodide solution, which dissolves the iodine, and the solution is titrated with sodium thiosulphate.

EXAMPLE.—The vapour density of hexane:

Weight of empty bulb in air - - = 23·449 g.
,, ,, bulb and vapour at 15·5° - = 23·720 g.

Temperature of sealing = 110°; barometric pressure = 759 mm., unchanged throughout the experiment. Capacity of bulb by weighing filled with water = 178 ml.

Weight of air displaced by bulb *

$$= 178 \times \frac{273}{288{\cdot}5} \times \frac{759}{760} \times 0{\cdot}001295 = 0{\cdot}2178 \text{ g.}$$

∴ weight of *vacuous* bulb in air = 23·449 − 0·218 = 23·231 g.;

∴ ,, ,, vapour = 23·720 − 23·231 = 0·489 g.

Vol. at S.T.P. of vapour filling bulb at 110° and 759 mm.

$$= 178 \times \frac{273}{383} \times \frac{759}{760} = 126{\cdot}7 \text{ ml.}$$ (the expansion of the bulb on heating is neglected);

∴ normal density $D = 0{\cdot}489/0{\cdot}1267 = 3{\cdot}86$ g./lit.

∴ molecular weight = 22·4 × 3·86 = 86·46.

The drawbacks to Dumas' method are (i) the large quantity of substance required to displace the air of the bulb, and (ii) if the substance contains impurities of higher boiling point, these come off last and make the density too high.

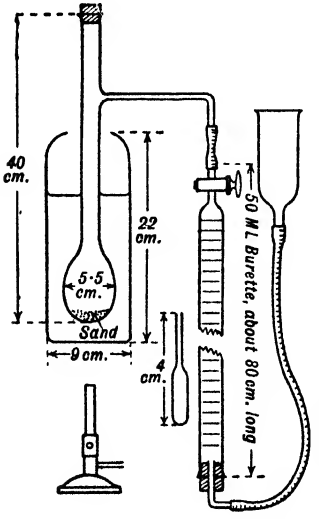


FIG. 7.—Victor Meyer's vapour density apparatus.

Victor Meyer's method.—In this so-called **displacement method** (1878) the volume of *air* displaced by a known weight of vapour is found. It is more rapidly and easily carried out than the Dumas or Hofmann method, requires only a small quantity of the substance, and can give quite accurate results.

A simple apparatus † which can be constructed in the laboratory is shown in Fig. 7. A weighed quantity of liquid in a small bulb is dropped into a bulb at the bottom of a wide vertical tube carrying a side tube delivering into an inverted burette filled with water and provided with a levelling funnel. The bulb and the lower part of the wide tube are heated in a vapour bath (an aluminium hot-water bottle with the top sawn off is shown) in which the temperature is constant and higher than the b.p. of the liquid but need not otherwise be known. As soon as the bulb is dropped in (a little sand is previously put in the large bulb

* Strictly speaking, the actual density of atmospheric air containing some carbon dioxide and moisture should be used. According to Kohlrausch it is usually sufficient to take as an average the density at S.T.P. as 0·001295.

† Palmer, *Experimental Physical Chemistry*, Cambridge, 1941, 22.

to avoid fracture) the rubber stopper at the top of the vertical tube is inserted. (The volume of air displaced into the burette by the stopper is previously found and subtracted from the total volume collected.)

The liquid rapidly volatilises and the vapour displaces its own volume of air at the temperature of the bath. This in turn displaces cooler air from the upper part of the tube, which collects in the burette. The tap is turned, the burette detached and moved to a place of constant temperature. After levelling again this volume of air is measured. It is essential that all the vapour must be contained in the bulb and part of the tube which are at the temperature of the bath, and that none diffuses into the cooler part of the tube. The volume of *dry* air collected is obviously equal to the volume which the vapour would occupy if it could exist at the atmospheric temperature and pressure.

EXAMPLE.—0·1008 g. of chloroform expelled 20·00 c.c. of moist air at 15° and 770 mm. pressure. Vapour pressure of water at 15° = 13 mm.

$$\therefore \text{ volume of dry air at S.T.P.*} = 20 \times \frac{273}{288} \times \frac{770 - 13}{760} = 18{\cdot}9 \text{ ml.}$$

$$\therefore \text{ normal density} = 1000 \times 0{\cdot}1008/18{\cdot}9 = 5{\cdot}333 \text{ g./lit.}$$

$$\text{molecular weight} = 22{\cdot}42 \times 5{\cdot}333 = 119{\cdot}6.$$

Victor Meyer's method is unsuitable for substances which dissociate on heating with increase of volume, such as phosphorus pentachloride :

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2,$$

since the vapour mixes with air in the bulb and its partial pressure is reduced to an *unknown* amount (p. 131).

Vapour densities at high temperatures.—The Dumas method was used at higher temperatures by Deville and Troost (1860), who used a porcelain bulb heated in the vapour of mercury, sulphur, stannous chloride, cadmium, or zinc, boiling in an iron bath, the tip of the bulb projecting through the lid being sealed off with an oxy-hydrogen blowpipe.

To find the temperature of the bulb, a companion bulb containing iodine, the density of the vapour of which at different temperatures is known, was placed alongside it in the bath.

Measurements by Victor Meyer's method at high temperatures were made by Nilson and Pettersson (1889), and by Biltz and V. Meyer, who used a bulb of glazed porcelain protected by wrapping with thick platinum foil and placed inside a graphite crucible heated in a Perrot's gas furnace. The bulb is filled with inert gas (nitrogen or argon) to prevent chemical action, and the substance, weighed out in a glass bulb, is dropped in as usual. Nernst (1903) used a Victor Meyer apparatus with an iridium bulb (3 c.c.) painted

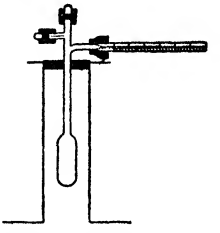


FIG. 8.—Nernst's vapour density apparatus.

* The equation holds if the tube and bulb were originally filled with *dry* air. If the partial pressure of water vapour in the air filling the tube and bulb at the beginning of the experiment was *h*, this is subtracted from the vapour pressure of water (13 mm. in the example). The difference does not usually exceed the experimental error.

outside with zirconia and heated electrically to 2000° in a small iridium tube furnace. The substance (usually a fraction of a milligram) was weighed on a microbalance, and the displacement measured by the movement of a drop of mercury in a horizontal graduated glass side tube (Fig. 8).

Abnormal vapour densities.—In some cases the measured vapour density differs from the normal value calculated from the molecular formula. When it is *greater* than the normal value it is assumed that the vapour contains more complex molecules, *i.e.* the substance is **associated.** When it is *less* than the normal value, the normal molecules have broken down into simpler molecules by **dissociation.**

This may often be proved experimentally, *e.g.* in the case of ammonium chloride by making use of the more rapid diffusion of ammonia as compared with hydrogen chloride (*College Course*, p. 95): $NH_4Cl = NH_3 + HCl$ (Pebal, 1862; Than, 1864). The formation of violet iodine vapour in the dissociation of the colourless gas hydrogen iodide: $2HI = H_2 + I_2$, of red bromine vapour in the dissociation of phosphorus pentabromide: $PBr_5 = PBr_3 + Br_2$, and of greenish-yellow chlorine in the case of phosphorus pentachloride: $PCl_5 = PCl_3 + Cl_2$, provide visible evidence of dissociation. The decomposition of associated into simpler molecules, *e.g.* of acetic acid: $(C_2H_4O_2)_2 = 2C_2H_4O_2$, is a special case of dissociation.

Dissociation (or *thermal dissociation*, to distinguish it from electrolytic dissociation) *is a reversible change brought about by heat, the products of which recombine on cooling.* When the chemical reaction is known, the *degree* (or *extent*) *of dissociation*, α, *i.e.* the fraction of the original normal substance which is dissociated, may be found from the gas or vapour density except in the case (*e.g.* $2HI \rightleftharpoons H_2 + I_2$) where there is no change of volume. The products of dissociation and the remainder of the undissociated substance are in equilibrium.

If each molecule of the normal (undissociated) substance forms n molecules on complete dissociation, then when the degree of dissociation is α, 1 g. mol. or mol of substance will have formed $n\alpha$ mols of dissociation products and $1 - \alpha$ mols of original substance will remain. The total number of mols in the gas is $(1 - \alpha) + n\alpha = 1 + (n - 1)\alpha$.

The volumes are in the ratio of the numbers of molecules (or mols) by Avogadro's hypothesis, and the densities are in the inverse ratio of the volumes. Hence if D is the density (g. per lit. at S.T.P.) of the normal (undissociated) substance and D' the density of the partly dissociated gas mixture, and V and V' the corresponding volumes:

$$\frac{V'}{V} = \frac{D}{D'} = \frac{1 + (n-1)\alpha}{1} = 1 + (n-1)\alpha,$$

from which α may be calculated. If $n = 2$, $D/D' = 1 + \alpha$. The *relative densities* (p. 7) (referred to H = 1 or O = 16 or air = 1 at *any* temperature) are sometimes given instead of the normal densities, and the ratio is the same in both cases.

The abnormal vapour densities of ammonium chloride, phosphorus pentachloride, ammonium carbamate, etc., led Deville to question the validity of Avogadro's hypothesis, but the true explanation that dissociation occurs was put forward by Cannizzaro in 1857, and independently by Kopp and by Kekulé in 1858.

In cases where no change of density occurs on dissociation the degree of dissociation may sometimes be found by other methods, *e.g.* in the case $2HI \rightleftharpoons H_2 + I_2$ by *rapidly* cooling the gas mixture, when very little recombination occurs, dissolving the solid iodine in potassium iodide solution, and titrating with thiosulphate.

EXAMPLE 1.—At 200° and 1 atm. pressure the normal density of phosphorus pentachloride is $D' = 6{\cdot}254$ g./lit. The normal density corresponding with no dissociation (PCl_5) is $D = 9{\cdot}308$ g./lit.

$$\therefore\ 1 + (n-1)\alpha = 1 + \alpha = 9{\cdot}308/6{\cdot}254\ ; \quad \therefore\ \alpha = 0{\cdot}489.$$

100 mols PCl_5 form 48·9 mols each of PCl_3 and Cl_2, leaving $100 - 48{\cdot}9 = 51{\cdot}1$ mols of PCl_5; hence the total number of mols in the gas is $51{\cdot}1 + 2 \times 48{\cdot}9 = 148{\cdot}9$. The *volume percentage* of PCl_3 or Cl_2 in the mixture is $100 \times 48{\cdot}9/148{\cdot}9 = 32{\cdot}84$, and of PCl_5 $100 \times 51{\cdot}1/148{\cdot}9 = 34{\cdot}3$ $(= 100 - 2 \times 32{\cdot}84)$.

The mol. wts. are $PCl_5 = 208{\cdot}5$, $PCl_3 = 137{\cdot}5$, $Cl_2 = 71$, hence the total weight of gas mixture from 100 mols of PCl_5 is :

$$100 \times 208{\cdot}5 = 51{\cdot}1 \times 208{\cdot}5 + 48{\cdot}9 \times 137{\cdot}5 + 48{\cdot}9 \times 71,$$

and the *weight percentage* of PCl_3 is $48{\cdot}9 \times 137{\cdot}5/208{\cdot}5 = 32{\cdot}25$.

EXAMPLE 2.—At 120° the vapour density of acetic acid is 44·75 (O = 16).

The mol. wt. of $C_2H_4O_2$ is 60. If the associated molecule is *assumed* to be $(C_2H_4O_2)_2$, this is partly dissociated $(C_2H_4O_2)_2 \rightleftharpoons 2C_2H_4O_2$.

$$\therefore\ \frac{D[\text{density of } (C_2H_4O_2)_2]}{D'[\text{density of partly dissoc. acid}]} = \frac{60}{44{\cdot}75} = 1 + \alpha.$$

$\therefore\ \alpha = 0{\cdot}3408$. Hence the **degree of association** is $1 - \alpha = 0{\cdot}6592$.

ATOMIC WEIGHTS

Determination of atomic weights.—When the **equivalent** of an element has been accurately determined by a chemical (or electrochemical, see p. 98) method, the **atomic weight** is given by the relation :

$$\textbf{Atomic weight} = \textbf{Equivalent} \times n,$$

where n is usually a small whole number. If an *approximate* atomic weight can be found, n is fixed and the *accurate* atomic weight can then be calculated from the equivalent. The approximate atomic weight may be found in several ways :

(1) **Cannizzaro's principle** (1858) : *the atomic weight of an element is the smallest weight contained in a molecular weight of any of its compounds.* In applying this, several compounds are analysed and their molecular weights determined by one of the following methods :

(i) *gas or vapour densities* ;

(ii) *diffusion or effusion and the use of Graham's law* (p. 30) ;

(iii) *osmotic pressure, lowering of vapour pressure, elevation of boiling point, or depression of freezing point, in dilute solutions of non-electrolytes* (Chap. III).

(2) The **ratio of the specific heats** of a gas or vapour at constant pressure (c_p) and at constant volume (c_v), $\gamma = c_p/c_v$, according to the kinetic theory (p. 33), is 1·667 for a monatomic gas and 1·400 for a diatomic gas with rigid ("dumb-bell") molecules.

For mercury vapour Kundt and Warburg (1876) found $\gamma = 1{\cdot}667$, hence it is monatomic. The vapour density gives the molecular weight 200, which must also be the atomic weight, as is found also from Cannizzaro's principle. The values of γ for argon and other inert gases are also 1·667, hence these gases are monatomic. The values for oxygen, hydrogen, nitrogen, nitric oxide, carbon monoxide and hydrogen chloride are 1·40, hence these gases have rigid diatomic molecules and have the formulae O_2, H_2, N_2, NO, CO and HCl, which is in agreement with Avogadro's reasoning. The values for chlorine gas and for bromine and iodine vapours are abnormally small (1·36), and these gases have diatomic molecules in which the two atoms are vibrating along the line of centres (p. 34).

(3) Dulong and Petit's **law of atomic heats** (1819) gives the *approximate* atomic weight of a *solid* element such as sulphur or a metal. The **atomic heat** is *the product of the atomic weight* (A) *and specific heat* (c): Atomic heat $= Ac$, and *for solid elements the atomic heat is approximately* 6·3. Hence $A = 6{\cdot}3/c$.

Dulong and Petit expressed the law in the form (*Ann. Chim.*, 1819, **10**, 395) that: "the atoms of all simple bodies have exactly the same capacity for heat."

Dulong and Petit's law is only approximate (see p. 224), and it does not apply to solid elements of low atomic weight and high melting point (such as carbon, boron and silicon), which have abnormally small atomic heats. It does not apply to gases.

(4) Mitscherlich's **law of isomorphism** (1819) states that *compounds having analogous formulae* (*e.g.* Fe_2O_3 and Cr_2O_3; $CaCO_3$ and $PbCO_3$) *crystallise in the same form, i.e.* are *isomorphous* (p. 235). The formula of a compound is thus found by comparison with that of an isomorphous compound of known formula, and if the formula and percentage composition are known the atomic weight of one element in a compound can obviously be calculated.

(5) *The position of an element in the* **periodic table** gives the *approximate* atomic weight by comparison with those of adjacent analogous elements. The position in the periodic table is also fixed by the **atomic number** deduced from the X-ray spectrum (p. 191).

(6) *The formulae of compounds with similar* **chemical properties** *are usually analogous.* This method is not always satisfactory, *e.g.* the formula of beryllium oxide BeO was once thought to be Be_2O_3 because of the resemblance in chemical properties to aluminium oxide Al_2O_3, and the rare earths M_2O_3 were formulated MO because they are often strong bases like MgO.

Accurate atomic weights by chemical methods.—Some elementary laboratory methods for the determination of *equivalents* (*College Course*, p. 74;

Intermediate Chemical Calculations, Ch. IV) are capable of refinement for use in accurate work. Atomic weights were determined (from the equivalents) by gravimetric methods in an increasing order of accuracy by Berzelius (1811–12), Stas (1860–65), and more recently by T. W. Richards and his pupils Baxter, Hönigschmid, etc.; and by physico-chemical methods (including gas densities) by Regnault, Morley, Guye, and R. Whytlaw-Gray and their pupils. The atomic weight of hydrogen was the subject of accurate researches by Dumas, Scott, Morley, and Burt and Edgar (p. 667).

The methods used for the **determination of equivalents** include:

(1) *Combination with or displacement of hydrogen.* This was used for chlorine in accurate researches (p. 781), and less accurately for some metals which displace hydrogen from acids or alkalis.

(2) *Combination of an element with oxygen* directly or by oxidation (*e.g.* with nitric acid), *or analysis of an oxide, e.g.* by reduction in hydrogen. Although oxygen is the standard of atomic weights, it should be borne in mind that only rarely can an oxide be obtained sufficiently pure for accurate work. Since a large number of atomic weights are found by methods involving a knowledge of the atomic weight of silver, Baker and Riley (*J.C.S.*, 1926, 2510) attempted to determine the ratio 2Ag : O by the analysis of silver oxide, but found it impossible to prepare this in a pure state. The method has been used for gaseous oxides of nitrogen (p. 573).

(3) *The combination of an element with chlorine,* directly or by precipitation of the chloride, *or the analysis of a chloride.* This method has been used for several metals, and if the atomic weight of silver is assumed, a known weight of a chloride of a metal or non-metal (B, P, etc.) is precipitated as silver chloride; the ratio *element* : *chlorine* can then be calculated. Bromine and iodine compounds are also used.

(4) *The weight of silver required to precipitate a known weight of a halogen compound.* This is a modification of method (3).

(5) *A known weight of one compound is converted into a determined weight of another compound. E.g.* an oxide MO is converted into a sulphate MSO_4 by treatment with sulphuric acid, when the ratio gives the atomic weight of M if the atomic weight of sulphur (32) is known: $\frac{M+32+64}{M+16}$.

(6) *Replacement of a metal* (*e.g.* copper) *from a solution of one of its salts by means of another metal* (*e.g.* zinc). This does not usually give accurate results, as the reaction is not quantitative.

(7) *Electrolytic deposition* of a metal (Faraday's law).

Stas's atomic weight determinations.—Stas's researches, published in 1860 and 1865 (*Œuvres complètes*, Brussels, 1894, vol. **1**; Mallet, *J.C.S.*, 1893, **63**, 1, or *Chemical Society Memorial Lectures*, 1901, **1**, 1), increased the accuracy attained in previous work (*e.g.* of Berzelius, Turner and Dumas), and introduced several general methods which are still in use. The correction of weights to a vacuum had been used by Turner (1833).

I. Stas heated a known weight of pure potassium chlorate in a hard glass flask: $KClO_3 = KCl + 1\frac{1}{2}O_2$. Berzelius (1818, 1826) and Marignac (1842), who had used this reaction, found that some solid $KClO_3$ and KCl were carried

away by the oxygen, and some chlorine (equivalent to 0·003 g. AgCl for 50 g. of $KClO_3$) was evolved. Stas plugged the neck of the flask with asbestos, which retained the $KClO_3$ and KCl carried off, and was afterwards heated to decompose the $KClO_3$; and he then passed the oxygen over heated precipitated silver in a weighed tube, which absorbed the chlorine evolved. After correcting for this he calculated that 74·590 g. of KCl was combined with 48 (= 3 × 16) g. of oxygen in the chlorate. This is the molecular weight of KCl.

Stas also used Penny's method (*Phil. Trans.*, 1839, **129**, 13 ; cf. Berry, *J.S.C.I.*, 1932, **51**, 453) of repeatedly evaporating a known weight of $KClO_3$ with concentrated hydrochloric acid to convert it into KCl. Penny had used a very simple apparatus of two flasks placed horizontally, one containing the reagents and heated on a sand-bath and with its neck inserted in the other flask. This method was also used by Stähler and Meyer (1911), who found $KClO_3 : KCl = 1·643819$.

II. Marignac (1846), by precipitating a known weight of pure KCl in solution with a slight excess of silver nitrate, and weighing the silver chloride :

$$KCl + AgNO_3 = AgCl + KNO_3,$$

calculated that 74·590 g. of KCl gave 143·39 g. of AgCl, the molecular weight.

III. Stas converted a known weight of pure silver into chloride (*a*) by heating the metal in a current of chlorine gas in a hard glass tube (a method used by Dumas in 1859), (*b*) by dissolving the silver in nitric acid and precipitating as silver chloride. He calculated that 107·94 g. of Ag gave 143·39 g. of AgCl, and thus 107·94 is the atomic weight of silver (Ag = 107·94).

$$\therefore \quad Cl = AgCl - Ag = 143·39 - 107·94 = 35·45,$$
$$K = KCl - Cl = 74·59 - 35·45 = 39·14.$$

Similar methods gave the atomic weights of sodium, bromine and iodine.

IV. To find the atomic weight of nitrogen, Stas used three methods :

(i) To a known weight of pure silver previously dissolved in dilute nitric acid in a stoppered bottle, a weighed amount of pure solid ammonium chloride was added, nearly sufficient to precipitate the silver, and the slight excess of silver was titrated with 0·1 *N* NaCl. This gave $Ag : NH_4Cl = 100 : 49·600$.

(ii) A weighed amount of KCl was converted into KNO_3 by repeated evaporation with nitric acid, and a weighed amount of KNO_3 converted into KCl by repeated evaporation with hydrochloric acid (Penny's method). Stas calculated the ratio $KCl : KNO_3 = 74·59 : 101·175$.

(iii) A weighed amount of pure silver was dissolved in nitric acid, the solution evaporated and the silver nitrate fused and weighed. Stas calculated the ratio $Ag : AgNO_3 = 100 : 157·484$.

From (i) : $\dfrac{107·94}{(N + 4H) + 35·45} = \dfrac{100}{49·60}$; $\therefore \quad NH_4 = 18·088.$

From (ii) : $\dfrac{74·59}{39·14 + N + 48} = \dfrac{74·59}{101·175}$; $\therefore \quad N = 14·035.$

From (iii) : $\dfrac{107·94}{107·94 + N + 48} = \dfrac{100}{157·484}$; $\therefore \quad N = 14·050.$

The first value is abnormally high, probably because of occlusion of ammonium chloride in the silver chloride, which is perceptible when the solid salt is added to the solution. The mean of all Stas's values for nitrogen was 14·04, which is too high, the true value being 14·008. The real basis of Stas's values is Ag = 107·94.

Richards' atomic weight researches.—T. W. Richards in 1904 repeated some of Stas's experiments (*J.A.C.S.*, 1905, **27**, 459; "Faraday Lecture," *J.C.S.*, 1911, **99**, 1201; "Memorial Lecture on Richards," *J.C.S.*, 1930, 1937; and Friend, *Text-Book of Inorganic Chemistry*, 1917, **1**, 241). Richards pointed out several sources of error in Stas's experiments: (i) the solubility of silver chloride; (ii) impurities dissolved from glass vessels; (iii) occlusion of oxygen in Stas's silver; (iv) occlusion of *soluble* salts in precipitated silver halides, especially when *solid* soluble halides were added to the silver solution; (v) the use of too large quantities of materials, making adequate washing of precipitates difficult; (vi) even carefully purified potassium chlorate always contains some chloride.

Richards profited by the improved laboratory facilities which had become available since Stas's time, particularly in purifying materials, especially the silver, which was fused in an atmosphere of hydrogen; he used platinum or quartz vessels, electric heating, and a centrifuge for separating solids from liquids. Richards also invented two important new devices, the *bottling apparatus* and the *nephelometer*.

(1) The **bottling apparatus** (Fig. 9) is a hard glass or quartz tube *A* fitted by a ground joint to a soft glass tube *B* with a pocket *C*. A platinum boat containing

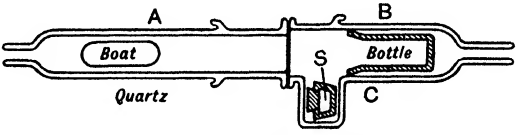


FIG. 9.—Bottling apparatus.

the substance was heated in *A* in a current of a gas, the weighing bottle being put into *B* with the stopper *S* in *C*. After cooling, the gas was displaced by dry air and the boat pushed into the weighing bottle, after which the stopper was similarly inserted. The bottle was then transferred to the balance. Hönigschmid's apparatus is similar, but the boat and stopper are moved by the action of a magnet on a bulb containing iron (*Z. anorg. Chem.*, 1929, **178**, 1).

(2) The **nephelometer** (Greek *nephele*, a cloud) determined traces of sparingly soluble substances such as silver chloride dissolved in the washings. In this case excess of silver nitrate was added, when (owing to the common ion effect, p. 168) a small amount of silver chloride was precipitated from the solution and an opalescence developed, which was compared with a standard in the nephelometer. This consists (Fig. 10) of two test-tubes containing the liquids and inclined in an inverted V, partly screened from bright light by two shutters, one moving over a scale. If the shade over the standard covered half the tube when the same appearance was seen from above, viewed through two flat prisms,

then a new standard about half as concentrated was put in, and a new comparison made. In this way the amount of suspended substance was accurately determined and a suitable correction applied. A different method was used by Briscoe *et al.* (*Proc. Roy. Soc.*, 1931, **133**, 440).

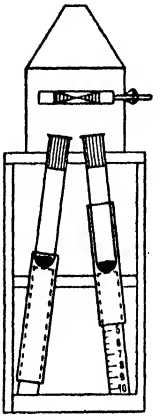


FIG. 10.—Nephelometer.

The work of Richards and his pupils, as well as the physico-chemical methods, changed the value for the atomic weight of silver from Stas's figure 107·94 to 107·88. Since it could not be directly referred to oxygen, the atomic weight of silver was found in a roundabout way.

Richards and Forbes (*J.A.C.S.*, 1905, **27**, 5) redetermined the ratio $Ag : AgNO_3$ by Stas's method, finding 100 : 157·479. With various *assumed* values for silver the corresponding atomic weights of nitrogen were calculated as :

Ag - -	107·93	107·89	107·88
N - -	14·037	14·014	14·008

Since accurate physico-chemical methods (limiting densities, etc.) had given the value N = 14·008, silver must be taken as Ag = 107·88 to agree with these.

Hönigschmid in 1927 (*Z. anorg. Chem.*, 1927, **163**, 65) found the same value for the ratio $Ag : AgNO_3$ by the dry reduction of silver nitrate to metallic silver. Hönigschmid and Sachtleben (*Z. anorg. Chem.*, 1929, **178**, 1) first referred silver independently to oxygen by (i) converting a known weight of pure barium perchlorate into chloride by heating in hydrogen chloride gas, thus finding the ratio $Ba(ClO_4)_2 : BaCl_2$, or $BaCl_2 : 8O$ (the solids were weighed in vacuum to avoid errors due to adsorbed gas), (ii) precipitating the barium chloride as silver chloride and so finding the ratio $BaCl_2 : 2AgCl$. From the two ratios they calculated Ag = 107·880 with reference to O = 16·000. This value is now accurately known, and as in the majority of cases atomic weights are determined relative to silver as a secondary standard, this is very important.

CHAPTER II

THE KINETIC THEORY

The Kinetic Theory of Gases

Experiments show that the particles of gases and liquids are in motion. Dalton in 1801 connected by a long vertical tube a bottle filled with hydrogen and another filled with carbon dioxide, the light gas being above (Fig. 11). After several hours the gases had uniformly mixed. This spontaneous mixing of gases (in opposition to gravity) is called **diffusion**, and is due to the *motion of the molecules* amongst each other.

Fig. 11.—Dalton's experiment on gaseous diffusion.

Similar motions occur in liquids. A tall cylinder is filled with water and a layer of copper sulphate crystals placed at the bottom. A layer of blue solution is formed. In a room of uniform temperature (to avoid convection currents) the blue colour slowly rises until, after several months, the colour of the whole liquid becomes uniform.

The assumption that *the molecules of liquids and gases are in ceaseless motion* is called the **kinetic theory** (Greek *kinesis*, motion).

Quantitative application of the kinetic theory to gases was made by Bernoulli (1738) and Joule (1848), and was developed especially by Clausius and Clerk Maxwell in the nineteenth century. An important memoir on the subject by Waterston, presented to the Royal Society in 1845, contained some errors and was not published until 1892, when it was discovered in the archives of the Society by Lord Rayleigh.

Joule in 1845 found that when a gas expands from one vessel into a second vacuous vessel, so that it does no *external* work, it is not as a whole appreciably warmed or cooled. He concluded that no *internal* work was done, and hence that *the molecules of gases exert practically no forces on one another.*

The pressure exerted by a gas must, then, be due to *molecular bombardment.* A ceaseless hail of elastic molecules impinges on the surface of the vessel, and the colliding molecules rebound into the gas. The molecules strike the wall at all angles, but only the component velocity normal to the surface is effective in causing pressure.

In the gas, the molecules move in straight lines until they hit the walls or collide with one another. The molecular collisions are relatively scarce compared with collisions with the walls, because the particles are very small and rather sparsely distributed, except in highly compressed gases.

The molecules may have all possible speeds, but Clerk Maxwell (1859) showed that the majority at a given temperature have speeds differing only

slightly from a **mean speed** $\bar{c}$ or Ω. The ordinates in Fig. 12 represent the *fractions* of the molecules with speeds represented by the abscissae. The

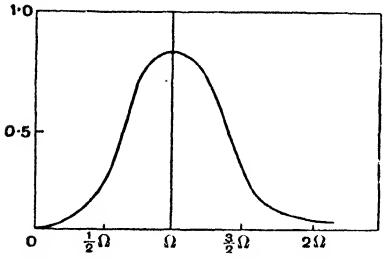


FIG. 12.—Distribution of molecular speeds in a gas.

component velocities fluctuate as the molecules collide, but the speed along the path of motion is nearly uniform.

Calculation of the pressure of a gas.—Let a mass M of gas be contained in a cube of side L, and let c be the speed of the molecules, assumed provisionally to be the same for all. Let there be N particles in a unit cube or NL^3 in the given cube. We assume that on the average one-third of the particles ($NL^3/3$) move (in *both* directions) perpendicular to each pair of faces.

The number of impacts per second by a particle on any one face is $c/2L$, since it traverses a distance $2L$ between each impact with that face. The total number of impacts per second on the face is $c/2L \times (NL^3/3) = NcL^2/6$. The momentum of the molecule of mass m before impact is mc, after impact it is $-mc$, hence the change of momentum is $2mc$. The *pressure* (change of momentum per sec. per sq. cm.) is $(NcL^2/6) \times 2mc \div L^2$, where L^2 is the area of the face.

$$\therefore\ p = \tfrac{1}{3}mNc^2. \qquad \text{.....(1)}$$

Actually the molecules have different speeds, but if N_1 have the speed c_1, N_2 the speed c_2, and so on, equation (1) applies to each kind and

$$p = \tfrac{1}{3}m\Sigma N_1 c_1^2.$$

If we define a mean square speed $\overline{c^2}$ such that

$$\Sigma N_1 c_1^2 = \overline{c^2}\Sigma N_1 = N\overline{c^2},$$

then

$$p = \tfrac{1}{3}mN\overline{c^2}. \qquad \text{.....(2)}$$

But mN = mass of gas per c.c. $= M/V = D$ = density ;

$$\therefore\ p = \tfrac{1}{3}D\overline{c^2} \quad \text{or} \quad pV = \tfrac{1}{3}M\overline{c^2}. \qquad \text{.....(3)}$$

The mass of gas striking one sq. cm. of wall per second $= \frac{1}{2}mN\bar{u} = \frac{1}{2}D\bar{u}$ where $\bar{u}$ is the mean molecular velocity normal to the wall. It can be shown that if the **mean speed** of the molecules is $\bar{c}$, the average component in any direction is $\frac{1}{2}\bar{c}$, and $\sqrt{\overline{c^2}} = \sqrt{\frac{3\pi}{8}}\,\bar{c} = 1{\cdot}086\bar{c}$. $\sqrt{\overline{c^2}}$ is called the **root mean square speed**, and is such that the total kinetic energy of translational motion of the molecules is $\frac{1}{2}\overline{c^2}$ per g.

Molecular energy.—The **kinetic energy of translation** of a molecule is $\frac{1}{2}m\overline{c^2}$, hence equation (3) shows that *the product of the pressure and volume of a gas is equal to two-thirds of the total kinetic energy of translation of the molecules*, since $\frac{1}{3}M\overline{c^2} = \frac{2}{3}(\frac{1}{2}M\overline{c^2})$. Only the translational motion of the molecules con-

tributes to the pressure of the gas, the rotation or the relative motion of the parts of molecules being without influence on this.

From Boyle's law, $pV = \text{const.}$ when the temperature is constant, and equation (3), it follows that *the kinetic energy of translation depends only on the temperature of the gas, not on its volume.* This is equivalent to Joule's law, from which we started.

Now put $M = \mathbf{M}$, the gram-molecule (mol) of the gas, and $N = \mathbf{N}$, the number of molecules in a gram-molecule. Avogadro's hypothesis shows that $\mathbf{N}$ is the same for all gases, and it is called **Avogadro's number.** Its value (p. 46) is $6{\cdot}03 \times 10^{23}$. Then *the kinetic energy of translation of the molecules is the same for a mol of any gas at a given temperature.* For, kinetic energy $= \frac{1}{2}\mathbf{M}\overline{c^2} = \frac{3}{2}pV_m$ from (3). But V_m is the same for a mol of any gas at a given pressure and temperature, and by Boyle's law pV is constant at a given temperature.

At S.T.P., $V_m = 22{\cdot}415$ litres $= 22{\cdot}415 \times 1000{\cdot}028$ cu. cm.,
$p = 760$ mm. Hg $= 76 \times 13{\cdot}59545 \times 980{\cdot}616 = 1{,}013{,}225$ dynes per sq. cm.;
$\therefore\ \frac{3}{2}pV_m = 22{\cdot}415 \times 1000{\cdot}028 \times 1013225 \times \frac{3}{2} = 3{\cdot}407 \times 10^{10}$ ergs
(1 lit. $= 1000{\cdot}028$ cu. cm.).

Thus, the molecular energy of translation of a mol of any gas at 0° is large enough to raise a weight of about a ton through one foot.

Since $pV_m = \mathbf{R}T$, the **gas constant** in absolute units is (0° C. $= 273{\cdot}09°$ abs.). $\mathbf{R} = \frac{2}{3} \times 3{\cdot}407 \times 10^{10}/273{\cdot}09 = 8{\cdot}317 \times 10^7$ ergs/1° C. per mol. In thermal units (1 g. cal. $= 4{\cdot}184 \times 10^7$ ergs) it is $\mathbf{R} = 8{\cdot}317 \times 10^7/4{\cdot}184 \times 10^7 = 1{\cdot}988$, or very nearly 2 g. cal./1° C. per mol.

Molecular speeds.—From the value of $\frac{1}{2}\mathbf{M}\overline{c^2}$, which is the same for all gases at a given temperature and equal (very approximately) to 34×10^9 ergs at 0°, we can calculate the molecular speeds.

For oxygen, $\mathbf{M} = 32$, $\therefore\ \overline{c^2} = 34 \times 10^9 \times 2/32$, $\therefore$ the **root mean square speed** $\sqrt{\overline{c^2}}$ at 0° C. $= 46{,}000$ cm. per sec. or 460 m. per sec. The **mean speed** $\bar{c}$ is $0{\cdot}921\sqrt{\overline{c^2}}$, *i.e.* 425 m. per sec. For hydrogen the mean speed at 0° is 1693 m. per sec.

MEAN MOLECULAR SPEEDS $\bar{c}$ AT 0° IN METRES PER SECOND

(Velocities of sound in the gases are given in brackets.)

Hydrogen 1693 (1286).	Oxygen 425 (317).
Helium 1202.	Carbon dioxide 362 (257).
Steam 565 (401).	Chlorine 285 (206).
Nitrogen 455 (337).	Mercury vapour 170.

Since $pV_m = \mathbf{R}T$ and $\frac{3}{2}pV_m = \frac{1}{2}\mathbf{M}\overline{c^2}$,

$$\therefore\ \tfrac{1}{2}\mathbf{M}\overline{c^2} = \tfrac{3}{2}\mathbf{R}T \qquad \text{.....(4)}$$

Hence *the translational energy is proportional to the absolute temperature*; per mol it is

$$\tfrac{3}{2} \times 8{\cdot}317 \times 10^7 T \text{ ergs} = 2{\cdot}982T \text{ g. cal.} \simeq 3T \text{ g. cal.}$$

Also $$\bar{c} = \sqrt{\frac{8}{3\pi}} \cdot \sqrt{\bar{c}^2} = \sqrt{8RT/\pi M},$$

which shows that *the mean speed $\bar{c}$ is proportional to the square root of the absolute temperature and inversely proportional to the square root of the molecular weight.*

For the same gas the value of $\bar{c}$ at any temperature T is found from the value at 0° C. by multiplying by $\sqrt{T/273}$. Hence the value at 1000° C. is $\sqrt{1273/273} = 2{\cdot}16$ times the value at 0°. The increase in speed with temperature is not rapid, and for a rise in temperature of 1000° from 0° the speed is only rather more than doubled.

For two different gases with molecular weights $\mathbf{M}_1$ and $\mathbf{M}_2$, at the same temperature, the mean speeds are in the ratio $\bar{c}_1/\bar{c}_2 = \sqrt{\mathbf{M}_2/\mathbf{M}_1}$. The speed of bromine molecules ($\mathbf{M} = 2 \times 80$) at 17° C. is

$$1700 \times \sqrt{290/273} \times \sqrt{2/2 \times 80} = 196 \text{ m. per sec.},$$

where 1700 is the speed of hydrogen molecules at 0° C.

The speeds of hydrogen and helium molecules are large compared with those of other gases. A speed of 1700 m. per sec. is over 5500 ft. per sec., or more than a mile per sec. It is seen from the table that the molecular speeds are of the same order as, but greater than, the **velocities of sound** u in the gases. The formulae $p = \frac{1}{3}D\bar{c}^2$ and $u = \sqrt{\gamma p/D}$ (p. 34), where $\gamma = c_p/c_v$, give $u = \sqrt{\frac{1}{3}\gamma} \cdot \sqrt{\bar{c}^2}$.

Effusion.—In effusion, studied by Graham, a gas is forced by pressure through a small aperture in a metal plate exposed to the air. *The rates of effusion of different gases are in the inverse ratio of the square roots of the molecular weights or densities.* It is possible to compare the molecular weights of different gases from the effusion rates. The apparatus, devised by Bunsen, is an **effusiometer.**

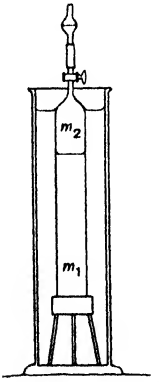


FIG. 13.—Bunsen's effusiometer (Ostwald).

EXPT. 1.—A glass cylinder with marks at m_1, m_2 is placed in a cylinder of water (Fig. 13). At the top is a stopcock with a tube closed by a thin platinum plate, in which a hole has been pierced with a fine needle. The tube is filled with gas to a level below m_1 and the tap opened. The gas streams out through the fine hole and the time for the liquid surface to pass from m_1 to m_2 is taken by a stop-watch. The experiment is repeated with a gas of known molecular weight, *e.g.* oxygen. The ratio of the squares of the times is the ratio of the densities or molecular weights: $t_2^2 : t_1^2 = D_2 : D_1 = \mathbf{M}_2 : \mathbf{M}_1$. If mercury is used, a float inside the tube, having a line marked on its upper end, is used. The time for this mark to pass between two marks on the upper surface of the cylinder is noted.

The law of effusion may be deduced independently of the kinetic theory. The work spent in forcing each gas through the aperture, represented by the

rise of level of the liquid, is the same, hence the kinetic energy imparted to each gas is the same. If u_1, u_2 are the velocities of *bulk* motion of the gases, *i.e.* the speeds at which the liquid level rises, we have :

$$\tfrac{1}{2}m_1u_1^2 = \tfrac{1}{2}m_2u_2^2,$$

where m_1 and m_2 are the masses of gas expelled. These occupy the same volume, hence $m_1/m_2 = D_1/D_2 = \mathbf{M}_1/\mathbf{M}_2$, where D is the density and $\mathbf{M}$ the molecular weight. Again, $u_1/u_2 = t_2/t_1$, where t is the effusion time. Hence :

$$t_2^2/t_1^2 = D_1/D_2 = \mathbf{M}_1/\mathbf{M}_2.$$

If the effusion is not isothermal this equation will not apply. In adiabatic effusion the ratio of specific heats $c_p/c_v = \gamma$ is involved.

Diffusion.—In spite of the high molecular speeds, *diffusion* of one gas into another is slow. Bromine vapour diffuses upwards into air in a cylinder only very slowly, although at 17° the speed of the bromine molecules is 196 metres per sec. The rate of bulk motion of bromine vapour is about one hundred thousandth of the molecular speed. The rate of diffusion in hydrogen is faster.

The molecules of bromine do not move in straight lines but collide with air molecules, and a great number must be deflected back towards the place from which they started. It is only after making a great number of collisions that a molecule can get appreciably forward.

This effect is due to the finite size of the molecules ; if they were mere points they would not offer any obstacles to the motion of other molecules. From the rate of diffusion the **diameters of molecules** may be calculated, but they are usually calculated from the viscosities of the gases (see below).

These diameters are all of the order of 10^{-8} cm. = 1 Ångström unit (A.) = 10^{-10} m. The values for assumed spherical molecules for some gases in A. are :

He	1·90	O_2	2·96	Kr	3·23
Ne	2·36	A	2·97	Xe	3·54
H_2	2·39	N_2	3·13	Cl_2	3·6

Platinum wires can be drawn to 10^{-4} cm. in diameter ; ordinary gold-leaf is 10^{-5} cm. thick ; the black parts of soap-films are 6×10^{-7} cm. thick, and oil-films on water are only 10^{-7} cm. thick, or even less.

The area exposed by the surfaces of all the molecules, assumed spherical, in 1 c.c. of oxygen at S.T.P., $4N\pi r^2$, is about 7 square metres.

The mean free path.—The mean distance traversed by a gas molecule between collisions is called its *mean free path*, L. This can be calculated from the **viscosity** η of the gas by the formula : $L = 1{\cdot}25\eta/\sqrt{pD}$. Since the density D is proportional to the pressure, L is inversely proportional to the pressure at a given temperature. At low pressures the molecules are further apart and the chance of collision is less. The viscosity is independent of pressure, an unexpected result deduced by Maxwell (1859) and confirmed experimentally. In air at 0° C. L in mm. is approximately $0{\cdot}1/p_{mm}$.

From the mean free path the **molecular diameter** d is calculated by the formula

$$L = \frac{1}{\sqrt{2}\pi N d^2},$$

where N = number of molecules per c.c. (*Loschmidt's number.*)

In oxygen at S.T.P., L is very nearly 10^{-5} cm.; it is double this in hydrogen. At low pressures, *e.g.* in the spaces between the walls of a "thermos" flask, the free path is several cm., and a molecule rebounds from the opposite walls many times without encountering another.

During one second a molecule describes as many free paths as it makes collisions, and the sum of the paths is equal to the mean speed $\bar{c}$. Thus the number of collisions of one molecule with others in the gas per second, is $\bar{c}/L$. In oxygen at S.T.P. this is $4{\cdot}25 \times 10^4/10^{-5} = 4{\cdot}25 \times 10^9$. At very low pressures the mean free path is 1 cm., but even then there will be 10^5, or 100,000 collisions per second.

If there are N molecules per c.c. the number of collisions of the molecules per c.c. per sec. (the **collision frequency**) is $\frac{1}{2}N\bar{c}/L = \frac{1}{\sqrt{2}} N^2\pi d^2\bar{c}$. (The factor $\frac{1}{2}$ is inserted because in taking all the N molecules each collision is counted twice.)

Since (p. 30) $\bar{c} = \sqrt{8\mathbf{R}T/\pi\mathbf{M}}$,

the number of collisions per c.c. per sec. is

$$2N^2d^2\sqrt{\pi\mathbf{R}T/\mathbf{M}},$$

where $\mathbf{R} = 8{\cdot}3 \times 10^7$ erg/1°.

For two different kinds of molecules the number of collisions per c.c. per sec. is given by

$$\pi\left(\frac{d_1+d_2}{2}\right)^2 N_1N_2\sqrt{\bar{c}_1^2+\bar{c}_2^2} = 2N_1N_2\left(\frac{d_1+d_2}{2}\right)^2\sqrt{2\pi\mathbf{R}T}\sqrt{\frac{1}{\mathbf{M}_1}+\frac{1}{\mathbf{M}_2}},$$

where d_1, d_2 are the diameters, N_1 and N_2 the numbers per c.c., $\bar{c}_1$, $\bar{c}_2$ the average velocities at the given temperature, and $\mathbf{M}_1$ and $\mathbf{M}_2$ the molecular weights.

Since the molecular speeds are inversely as the square roots of the densities (or molecular weights, at the same temperature and pressure), it can be anticipated that *the rates of diffusion of gases are inversely proportional to the square roots of the densities* (**Graham's law of diffusion,** 1833). The diffusion rate, however, involves the mean free path as well as the molecular speed and the quantitative relation is rather complicated.

Table of Molecular Magnitudes

Number of molecules per c.c. of gas at S.T.P. $= N = 2{\cdot}69 \times 10^{19}$.
Number of molecules per gram-molecule (22·415 litres in ideal state at S.T.P.) $= \mathbf{N} = 6{\cdot}03 \times 10^{23}$.
Mass of hydrogen atom $= 1{\cdot}69 \times 10^{-24}$ g.
Mean speed of hydrogen molecule at 0° = 1693 m./sec.
Translational kinetic energy of a molecule at 0° $= 5{\cdot}66 \times 10^{-14}$ erg.
Rate of change of translational kinetic energy per 1° $= 2{\cdot}056 \times 10^{-16}$ erg/degree.
Diameter of hydrogen molecule $= 2{\cdot}4 \times 10^{-8}$ cm.

Mean free path of hydrogen molecules at S.T.P. $= 1{\cdot}22 \times 10^{-5}$ cm.
Average distance apart of gas molecules at S.T.P. $= 3 \times 10^{-7}$ cm.
Number of collisions per second of oxygen molecules per c.c. at S.T.P. $= 5{\cdot}85 \times 10^{28}$.
Time of describing free path of oxygen molecules at S.T.P. $= 2{\cdot}3 \times 10^{-10}$ sec.

Thermal Magnitudes

The specific heats of a gas.—When 1 mol of a gas is heated *at constant volume* from $T°$ to $(T+1)°$ abs. the heat absorbed is the **molecular heat at constant volume,** $C_v = \mathbf{M}c_v$ where $\mathbf{M}$ = molecular weight and c_v = specific heat at constant volume. When the gas is heated *at a constant pressure of* 1 *atm.* it expands, doing work against the atmospheric pressure, and the heat absorbed is the **molecular heat at constant pressure,** $C_p = \mathbf{M}c_p$.

For an ideal gas, no heat is absorbed in the change of *volume* alone (cf. p. 27), and the difference of molecular heats $(C_p - C_v)$ will be equal to the external work done, viz. (*pressure*) × (*increase of volume*).

$$\therefore\ C_p - C_v = p(V' - V) = pV\left(\frac{T+1}{T} - 1\right) = \frac{pV}{T} = \mathbf{R}.$$

In a **monatomic gas** the heat absorbed for 1° rise in temperature increases only the kinetic energy of translation of the molecules by the amount:

$$C_v = \frac{1}{T}\left(\frac{\mathbf{M}c^2}{2}\right) = \tfrac{3}{2}\mathbf{R} \simeq 3 \text{ g. cal.}$$

from equation (4). But $C_p = C_v + \mathbf{R} \simeq 3 + 2 = 5$ g. cal., hence the **ratio of specific heats** for a monatomic gas is

$$C_p/C_v = c_p/c_v = \gamma \simeq 5/3 = 1{\cdot}667.$$

If the molecule contains more than one atom, part of the heat supplied at constant volume is used in increasing the kinetic energy of **rotation** of the molecule, and in addition the energy of **vibration** of the atoms if the molecule is not rigid. If this total extra energy is E per 1° rise of temperature:

$$C_p/C_v = \frac{\frac{3}{2}\mathbf{R} + \mathbf{R} + E}{\frac{3}{2}\mathbf{R} + E} < \frac{\frac{3}{2}\mathbf{R} + \mathbf{R}}{\frac{3}{2}\mathbf{R}} < 1{\cdot}667.$$

The value of C_p/C_v at 15° for a gas, the molecules of which contain more than one atom, is found to be less than 1·667, as the table below shows.

		C_p/C_v			C_p/C_v
Helium	He	1·667	Carbon dioxide	CO_2	1·302
Oxygen	O_2	1·396	Nitrous oxide	N_2O	1·300
Nitrogen	N_2	1·405	Ammonia	NH_3	1·310
Hydrogen	H_2	1·411	Sulphur dioxide	SO_2	1·285
Carbon monoxide	CO	1·404	Hydrogen sulphide	H_2S	1·340
Hydrogen chloride	HCl	1·400	Methane	CH_4	1·310
Chlorine	Cl_2	1·355	Ethylene	C_2H_4	1·250

The **theory of equipartition of energy** (Maxwell; Boltzmann) states that *the average kinetic energy of a molecule is shared equally among the degrees of freedom of motion.*

A *monatomic molecule*, regarded as a smooth sphere, has three degrees of translational freedom (along the x, y, z axes) and its rotational energy is assumed to be constant and unchanged by collisions (since the molecule is smooth). Hence the kinetic energy per degree of freedom is one-third of the total, or $\frac{1}{3} \times (\frac{3}{2}\mathbf{R}T) = \frac{1}{2}\mathbf{R}T$, from equation (4). A *rigid diatomic molecule*, regarded as a dumb-bell structure, has three degrees of translational freedom for its centre of gravity and three degrees of rotational freedom, two at right angles to one another, and one around the axis. It is assumed that the last motion is unchanged by collisions, so that there are two effective degrees of rotational freedom, or five degrees of freedom in all. The average kinetic energy of all the degrees of freedom is the same, hence the total kinetic energy is

$$(3+2) \times \tfrac{1}{2}\mathbf{R}T = \tfrac{5}{2}\mathbf{R}T.$$

The molecular heat at constant volume is thus $C_v = \frac{5}{2}\mathbf{R} = 5$ g. cal.,

$$\therefore\ C_p = 5 + \mathbf{R} = 7 \text{ g. cal.}, \quad \text{and} \quad C_p/C_v = \gamma = 7/5 = 1{\cdot}40.$$

The table shows that this value is found approximately for several diatomic gases, but hydrogen has an abnormally low value of C_v and hence γ is greater than 1·40. Chlorine has an abnormally high value of C_v (probably due to energy of vibration along the axis), and hence γ is abnormally low. Gases containing more than two atoms in the molecule have values of γ less than 1·4.

The value $C_p/C_v = 1{\cdot}667$ was found for mercury vapour by Kundt and Warburg in 1876, and confirmed the monatomic character of the mercury molecule (inferred from vapour densities and on chemical grounds). The method was used by Ramsay in the case of the inert gases argon, etc., for which no other method was available in the determination of the atomic weight. The molecules were found to be monatomic.

The value of γ for a gas is usually determined from the **velocity of sound** u:

$$u = \sqrt{\gamma p/D} = \sqrt{\gamma \mathbf{R}T/\mathbf{M}},$$

or by methods depending on the **adiabatic expansion** of the gas:

$$pV^{\gamma} = \text{const.}, \quad \text{or} \quad pT^{\frac{\gamma}{\gamma-1}} = \text{const.}$$

The theory of equipartition of energy is only approximately true for rotations and especially for vibrations; the parts of the specific heat due to these are temperature dependent. At low temperatures the rotational sp. ht. of the hydrogen molecule falls off and at about $-230°$ C. becomes zero. The molecular heat then has the value $C_v = 3$ for a *monatomic* gas. This is explained by the hypothesis that the energy of rotation is given by the quantum law, and at low temperatures decreases with temperature more rapidly than $\frac{1}{2}\mathbf{R}T$ for each degree of freedom of rotation. The effect is measurable only with hydrogen, but the temperature effect on the vibrational sp. ht. is measurable with most gases.

Imperfect Gases

The van der Waals equation.—Boyle's law $pV = const.$ is true only for an ideal (or perfect) gas, or for actual gases only at very low pressures ($p \to 0$) (see p. 11). Amagat's results for three gases are shown in Fig 14, in which $pV = 1$ corresponds with an ideal gas. It is seen that at all pressures pV for hydrogen is increasingly greater than 1, *i.e.* hydrogen is *less* compressible than an ideal gas (V greater than ideal for all values of p); while nitrogen and carbon dioxide are *more* compressible at moderate pressures, but become increasingly less compressible at high pressures. Hydrogen was called by Regnault *plus que parfait*, but all gases behave like it at high pressures.

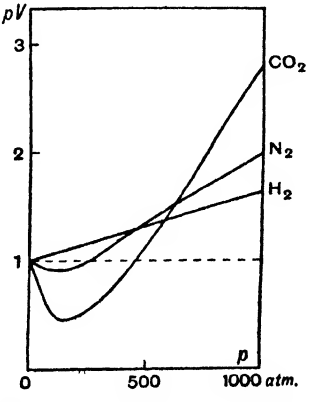


FIG. 14.— Isothermals of gases at high pressures.

These results may be explained by assuming that (i) *the gas molecules attract one another*, which makes the gas more compressible than an ideal gas, and (ii) *the gas molecules occupy a finite volume*, and so a highly compressed gas, in which the molecules are close together, tends to behave like a liquid, which is almost incompressible. In the case of hydrogen, effect (ii) outweighs effect (i) even at moderate pressures, since the molecular attraction is very small for this gas.

These two factors are taken into account by the **equation of van der Waals**, which replaces the ideal gas equation $pV = \mathbf{R}T$ by:

$$\left(p + \frac{a}{V^2}\right)(V - b) = \mathbf{R}T, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

where a and b are constants (see Jeans, *J.C.S.*, 1923, **123**, 3398). The term a/V^2 is the molecular attraction correction, which is inversely proportional to the square of the volume; it adds itself to the external pressure. The term b is the correction for the space occupied by the molecules. According to van der Waals, b is equal to four times the total volume of the molecules, but it appears to be $4\sqrt{2}$ times the latter. This equation gives good results with some gases (*e.g.* ethylene), but the attraction term depends on the temperature, hence D. Berthelot used the equation (p. 13):

$$\left(p + \frac{a'}{TV^2}\right)(V - b) = \mathbf{R}T,$$

which gives good results at moderate pressures, and has been given a theoretical foundation by Keesom (1912).

If we assume that the molecules are spherical and of radius r, we have $4 \times \frac{4}{3}\pi r^3 \mathbf{N} = b$. For oxygen, $b = 20{\cdot}8$ c.c. per mol,

$$\therefore\ r = \sqrt[3]{\frac{20{\cdot}8 \times 3 \times 7}{4 \times 4 \times 22 \times 6{\cdot}03 \times 10^{23}}} = 1{\cdot}27 \times 10^{-8}\ \text{cm.},$$

which is smaller than the value $1{\cdot}48 \times 10^{-8}$ calculated from the viscosity.

Critical constants.—Thomas Andrews in 1869 found that, when corresponding pressures and volumes of a fixed mass of carbon dioxide are plotted for various temperatures, the *isothermals* (constant temperature lines) shown in Fig 15 are obtained. At 48·1° the curve is a hyperbola corresponding with Boyle's law $pV = \text{const.}$; at 35·5° and 32·5° there are marked deviations, the gas being more compressible. At 31·1° the curve turns very rapidly at 75 atm., when it changes curvature at a point of inflexion and runs for a moment horizontal. Below 31·1° each curve has three parts, one on the right corresponding with the gas, a middle horizontal part where both liquid and gas are present at constant pressure, and a nearly vertical left-hand part corresponding with the almost incompressible liquid. These experiments show that a gas cannot be liquefied by the application of pressure unless its temperature is below a certain point, called the **critical temperature**. This is different for every gas. For carbon dioxide it is 31·1°.

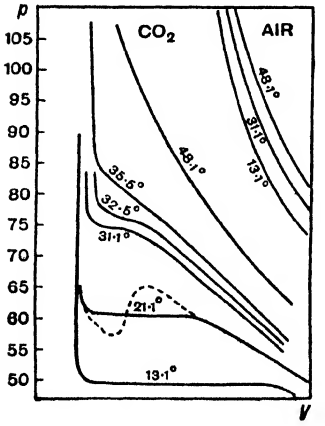


FIG. 15.—Isothermals of carbon dioxide. Critical phenomena.

The **critical temperature** t_c *of a gas is the highest temperature at which liquefaction can be caused by increase in pressure.* The **critical pressure** p_c is *the pressure which is just sufficient to liquefy the gas at the critical temperature.* The **critical volume** V_c is *the volume of* 1 *mol of the substance at the critical temperature and pressure.* The **critical point** is the point of inflexion on the critical isothermal corresponding with the critical pressure and temperature, and at this point the substance is in the **critical state.** For carbon dioxide, $p_c = 75$ atm., $t_c = 31{\cdot}1°$ C., and $V_c = 95{\cdot}6$ c.c.

At the critical point liquid and vapour must become identical, and in passing along (or above) the critical isothermal from right to left, it is possible to convert gas *continuously* into liquid without any separation into liquid and vapour phases, as on the horizontal parts of the lower isothermals. Cagniard de la Tour in 1822 had shown that when a liquid such as ether is heated in a sealed tube the liquid meniscus vanishes at a certain temperature and reappears at this temperature on cooling.

Van der Waals's equation (5) when multiplied out is a cubic equation in V:

$$V^3 - V^2\left(b + \frac{RT}{p}\right) + V\frac{a}{p} - \frac{ab}{p} = 0. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(6)$$

If the three roots are x_1, x_2, x_3, then

$$(V - x_1)(V - x_2)(V - x_3) = 0.$$

These three roots may all be real, or one may be real and the other two imaginary; hence for every p and T there are either one or three values of V. The first case corresponds with a gas. By plotting the equation for various values of T (as in the dotted curve), below the critical temperature, each isotherm cuts a horizontal line parallel to the V axis in *three* points, one corresponding with the liquid and one with the gas, whilst the third point lies between them and does not denote a real state, since the pressure increases with the volume. At the critical point, these three points coalesce at the point of inflexion of the curve, *i.e.* the three roots become equal and $x_1 = x_2 = x_3 = V_c$;

$$\therefore\ (V - V_c)^3 = V^3 - 3V^2V_c + 3VV_c^2 - V_c^3$$
$$= V^3 - V^2\left(b + \frac{RT_c}{p_c}\right) + V\frac{a}{p_c} - \frac{ab}{p_c}.$$

By equating coefficients of like powers of V and rearranging, we find the values of the critical constants in terms of a and b, which can be found from the compressibility of the gas:

$$V_c = 3b, \quad p_c = \frac{a}{27b^2}, \quad T_c = \frac{8}{27}\frac{a}{bR}. \qquad \text{.....(7)}$$

Liquefaction of Gases

Since there are attractive forces between the molecules of gases, and these are greater the nearer the molecules are to one another, it can be expected that by bringing the molecules close together by strong compression, and reducing their velocities by strong cooling, they may condense to a liquid. Those gases which deviate most from Boyle's law by being more compressible than ideal gases are most easily liquefied.* Ammonia was liquefied in 1799 by cooling and compression by Van Marum, Fourcroy and Vauquelin, and Guyton de Morveau; sulphur dioxide by cooling by Monge and Clouet about 1800, and sulphur dioxide, chlorine and hydrogen chloride by compression by Northmore in 1806.

At the suggestion of Davy, chlorine hydrate (p. 776) was heated in a sealed tube by Faraday in 1823 and liquid chlorine obtained. Davy liquefied hydrogen chloride, and Faraday liquefied hydrogen sulphide, carbon dioxide, sulphur dioxide, nitrous oxide, ammonia and cyanogen. The materials producing the gas were warmed in one limb of a strong sealed glass tube (Fig. 16), the other limb, in which the liquefied gas collected, being cooled in a freezing mixture.

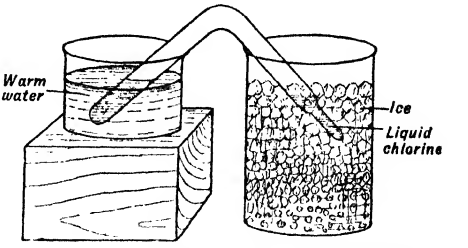


FIG. 16.—Liquefaction of chlorine by Faraday.

* Some gases are liquefied at atmospheric pressure by moderate cooling (e.g. with a freezing mixture of ice and crystalline calcium chloride at −40°):

Sulphur dioxide	−10°	Ammonia	−33·5°
Cyanogen	−21°	Chlorine	−34·5°

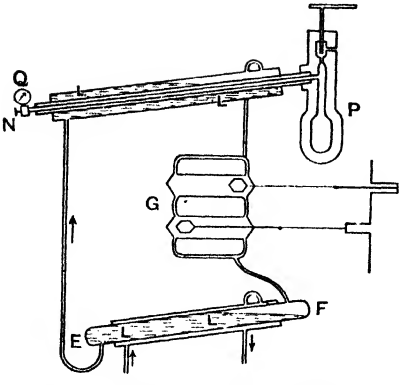


FIG. 17.—Liquefaction of oxygen by Pictet.

Thilorier in 1835 obtained liquid carbon dioxide in quantity in an iron apparatus and from it produced solid carbon dioxide by releasing the liquid into the air through a valve. By mixing solid carbon dioxide and ether he obtained a freezing mixture at $-78°$, and under reduced pressure the temperature was $-110°$.

Faraday in 1845 by using this cooling mixture and also high pressure was able to liquefy and even solidify many gases, but oxygen, nitrogen, carbon monoxide, nitric oxide, hydrogen and coal gas could not be liquefied by strong cooling and high pressures. Pressures up to 2000 atm. had been tried without success by Natterer in 1844. After the work of Andrews (1869) had shown that there is a *critical temperature* for each gas, above which it cannot be liquefied by pressure, it was realised that the critical temperatures of these so-called "permanent gases" must be very low and that very strong cooling would be necessary for their liquefaction. In this way oxygen was liquefied independently and almost simultaneously by Pictet and by Cailletet in December, 1877.

Pictet used the apparatus shown in Fig. 17. Oxygen generated in the retort *P* by heating potassium chlorate, was compressed by its formation in a copper tube, cooled in liquid carbon dioxide *L* boiling under reduced pressure, and fitted with a pressure gauge *Q* and release-valve *N*. The carbon dioxide was reliquefied by a pump *G* in a second copper tube *EF*, surrounded by liquid sulphur dioxide boiling under reduced pressure, and circulated by a second pump. Pictet reduced the temperature to $-140°$ and the pressure rose to several hundred atmospheres. On opening the release-valve *N*, a jet of liquid oxygen issued from it, at once boiling away.

Cailletet compressed the gas by a powerful pump forcing water into a strong steel vessel *B*, Fig. 18, in which the gas was contained in a tube *T* sealed below by mercury. Water forced into *B* drove the mercury into *T* and strongly compressed the gas. The pressure was suddenly released by opening a valve which allowed the water to escape, and the gas ex-

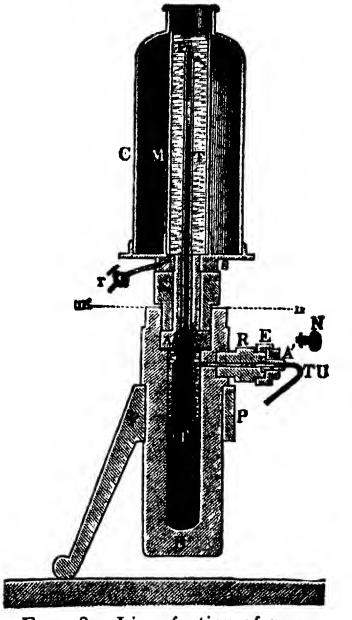


FIG. 18.—Liquefaction of gases by Cailletet.

panded suddenly (*adiabatic expansion*); the energy so spent in doing work against the atmospheric pressure was taken as heat from the gas and so cooled it. The cooling produced reached the point of liquefaction of the oxygen. A fog of liquid droplets was seen momentarily in the tube, at once vanishing as heat was communicated from the walls of the latter.

Pictet's method was used by Wroblewski and Olszewski in 1883 and by Dewar from 1884, the latter inventing the now familiar " thermos " flask.

Liquid air.—Air was first liquefied in bulk in 1895 independently by Hampson in England and by Linde in Germany, who made use of a new principle, viz. the **Joule-Thomson effect,** investigated by Joule and William Thomson (later

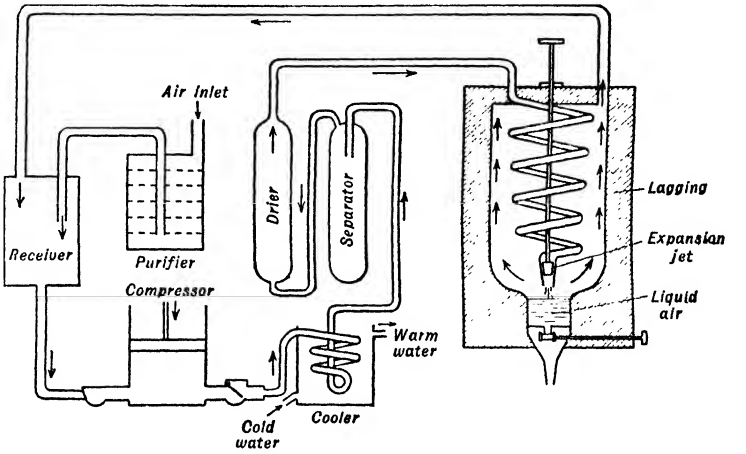


FIG. 19.—Production of liquid air.

The air is drawn by a pump through a purifier, and is compressed. The heat produced by compression is taken out by a cooler, and the air then passes through apparatus in which moisture is removed. The compressed air expands through a jet, and becomes cooled. The cold air sweeps over the pipe bringing the compressed air to the jet and cools it before expansion. The air finally becomes so cold that it liquefies.

Lord Kelvin) from 1852. When a compressed gas escapes into free air through an expansion valve, a slight cooling effect occurs with most gases (air, oxygen, nitrogen, carbon dioxide), but a slight heating effect with hydrogen at the ordinary temperature.

This temperature change is quite different from that due to the external work done by a gas in adiabatic expansion, and is due to the *internal* work spent in separating the molecules against their attractions. The energy required is taken as heat from the gas, and slight cooling results.

The Joule-Thomson cooling effect in degrees C. for air is given by

$$\frac{\text{difference of pressures in atm.}}{4} \times \left(\frac{273}{T}\right)^2,$$

where T is the absolute temperature before expansion.

If air at 0° C. and under a pressure of 100 atm. is expanded through a valve to atmospheric pressure, the fall of temperature will be 24·7°. If this cool air sweeps over the outer surface of a copper pipe bringing compressed air to the valve, the expanded air abstracts heat from the air coming to the valve. The cooled compressed air is further cooled by expansion, and so the cooling effect *accumulates*, and the air issuing from the nozzle finally becomes so cold that it liquefies.

This apparatus is called a **heat-interchanger** and was used by Hampson and by Linde for the liquefaction of air on a large scale. A diagrammatic representation of an air liquefaction apparatus, which is self-explanatory, is given in Fig. 19. In modern apparatus an expansion engine is used before the expansion valve, as explained on p. 654.

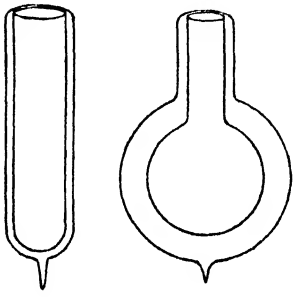


FIG. 20.—Vacuum vessels.

Liquid air is kept in double-walled Dewar (" thermos ") flasks (Fig. 20), the inner surfaces of which, silvered to reflect heat, have a high vacuum between them to cut down heat transmission.

Liquid air is usually slightly turbid from particles of ice and solid carbon dioxide. If filtered through a large filter paper it is a clear liquid, with a pale blue colour due to liquid oxygen. If poured out into the air it evaporates, producing thick white clouds of condensed moisture. Its temperature is about −190° and when exposed to this extreme cold many substances undergo remarkable changes in properties.

Lead becomes elastic and a lead bell rings when struck after cooling in liquid air. Rubber tubing becomes hard and brittle. Mercury is frozen to a malleable solid. Raw meat, fruits, etc., become hard, and can be reduced to powder in a mortar, and flowers can be crushed to powder in the hand. A kettle containing liquid air " boils " briskly on a slab of ice, and copious clouds of " steam," *i.e.* atmospheric moisture condensed to particles of ice by the cold of the escaping air, issue from the spout. The phosphorescence of calcium sulphide is quenched at the temperature of liquid air, but appears again on warming. Sulphur and mercuric iodide become much paler in colour on cooling in the liquid.

On standing, liquid air becomes bluer in colour ; the more volatile colourless nitrogen (b.p. −195·7°) escapes, and the liquid is enriched in pale-blue **liquid oxygen** (b.p. −182·9°).

A cigarette soaked in liquid oxygen burns rapidly when lighted ; a stick of carbon heated to redness, or a spiral of iron wire tipped with burning wood, burns brightly under the surface of liquid oxygen in a beaker, and with a little care a hydrogen flame continues to burn under the liquid, forming a strong smell of ozone.

Liquefaction of hydrogen.—Unlike other gases (except helium) hydrogen becomes slightly *warmer* on Joule-Thomson expansion at ordinary temperature, but when it is first strongly cooled (to −80·5° at 113 atm.) it shows the

normal Joule-Thomson effect and is further cooled by expansion. Thus, the effect has an *inversion temperature*, at which (for a given pressure) the effect changes sign. This is of great importance in the liquefaction of hydrogen (and helium).

Wroblewski and Olszewski in 1884–5 cooled hydrogen to $-183°$ and expanded it from 100 atm. pressure; they obtained some evidence of liquefaction by the formation of a fog, but liquid hydrogen in bulk was first obtained by Dewar at the Royal Institution in London (where Faraday's work was done) in 1895 (*Proc. Chem. Soc.*, 1896, **11**, 229). Olszewski in 1895 found that the critical temperature of hydrogen is $-234°$ (the accurate value is $-239{\cdot}9°$). Dewar cooled hydrogen to $-200°$ at 200 atm. pressure and expanded it through a valve, obtaining a colourless liquid, b.p. $-252{\cdot}78°$.

Liquid hydrogen is easily obtained by a modification of Travers' apparatus devised by Nernst (1911), shown in Fig. 21. Compressed hydrogen enters through the copper coil *A* and passes through an extension *A'* of the coil immersed in liquid air in a large Dewar vessel. The cooled gas then passes through *A''*, composed of two copper coils in parallel inside a small Dewar tube completely enclosed in a brass vessel *B*. At the end of this coil an expansion valve *V* is operated from outside. In *A''* the previously cooled gas is liquefied by the cold expanded gas from the valve sweeping over the coil, and liquid hydrogen collects in the inner Dewar vessel. The cold hydrogen gas passes out through a copper coil *C* wound in contact with *A*, and takes heat from the incoming hydrogen. The liquid air boiling in the outer Dewar vessel gives off cold air which passes out through a copper coil *D*, wound between *A* and *C*, and takes up heat from the incoming hydrogen. The brass vessel *B* is in two parts, screwed together, to permit of the inner Dewar tube being inserted. 300–400 c.c. of liquid hydrogen are obtained per hour with a gas velocity of 2–3 c.c. per second and the use of about 300 c.c. of liquid air.

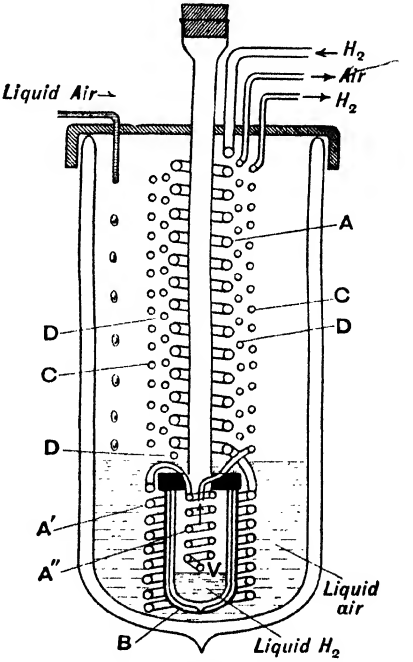


FIG. 21.—Preparation of liquid hydrogen.

At the temperature of liquid hydrogen all other gases except helium and neon are frozen to solids which at this extreme cold show practically no vapour pressure. If liquid hydrogen is poured into an ordinary test-tube a white coating of ice at once covers the outside. From this, drops of liquid air are seen to fall.

Liquids

The attractive forces exerted by molecules upon one another are considerable in the liquid state, when the molecules are close together.

Since the actual space occupied by spheres of radius r most densely packed is 0·74 of the total volume, if the molecules are in contact in a liquid :

$$\tfrac{4}{3}\pi r^3\mathbf{N} = 0{\cdot}74\,V$$

where **N** is Avogadro's number and V the molar volume (= mol. wt./density). This gives an *approximate* value of the molecular radius r.

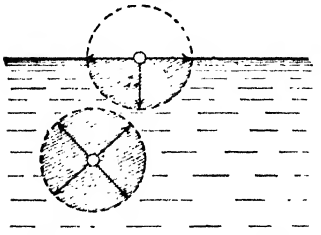


Fig. 22.—Range of molecular forces in a liquid.

A molecule in the *body* of a liquid is attracted equally in all directions, and the resultant force on it is zero. The range of the attractive forces is small ; van der Waals calculated it to be of the order of 10^{-6} cm. Molecules in the *surface*, however, are subject to a resultant attraction downwards and sideways, due to the unbalanced forces between the molecules in the surface and below it. Thus the surface molecules behave like a stretched elastic film tending to contract (Fig. 22). These forces give rise to **surface tension.**

The surface tension σ is measured by finding the height h cm. to which a liquid of density D g./c.c. rises in a capillary tube of radius r cm. when

$$\sigma = \tfrac{1}{2}grhD \text{ dynes/cm.},$$

where g = acceleration of gravity (981 cm. per sec. per sec.).

The attractive forces between molecules may act in one or two directions only, as if the molecules were small magnets. The molecules in the liquid surface will then mostly be arranged with the same parts pointing in one direction. Rayleigh (1899) found that the thinnest oil-films on water were unimolecular, and the formation of unimolecular films has been proved in many cases by Langmuir and by Harkins (from 1917). A drop of a solution of fatty acid or other insoluble substance in benzene is brought on a perfectly clean surface of water. The solvent evaporates, leaving an isolated patch of film. By bringing a strip of paraffined paper across the surface of the water so as to enclose the film between it and the sides of the trough, no resistance is encountered until the edges of the film touch the sides of the trough and the strip of paper. A pressure is now observed, and can be measured by a suitable apparatus. The area of the film is equal to the area A between the paper strip and the sides of the trough, and since the weight w of the film is known, the area a occupied by a single molecule in the unimolecular film is given by :

$$a = A\mathbf{M}/w\mathbf{N},$$

where **M** is the molecular weight of the substance in the film and **N** is Avogadro's number. The thickness t of the film can be calculated from the density D, assumed the same as that of the substance in bulk :

$$D \,.\, At = w.$$

It is found that for fatty acids R·COOH, a is practically the same with varying lengths of chains of carbon atoms R, so that the molecule is orientated in an upstanding position on the water surface, with the carboxyl group COOH of the acid immersed in the water and the carbon chain outside.

Evaporation.—Some molecules in a liquid, with more kinetic energy than the average on approaching the surface, have sufficient energy to break away from the attractive forces and evaporate. Escape of these molecules reduces the mean energy of the liquid, which becomes cooler. To keep the temperature constant, heat must be added ; this is the latent heat of evaporation.

Molecules in the vapour approaching the liquid are attracted near the surface. They describe curved orbits and are caught and dragged into the liquid with increased kinetic energy. Heat is therefore given out on condensation. When as many molecules enter as leave the liquid per second a state of equilibrium is reached corresponding with the saturation vapour pressure.

If the forces acting on liquid molecules are as shown in Fig. 22, the work done in bringing a molecule from the interior to the surface will be half that required to remove it from the liquid to the vapour space, the latter being measured by the internal latent heat of evaporation (Stefan, 1886). The *translational* kinetic energy of the molecule is the same in the liquid and vapour, since it depends only on the temperature.

Molecular weights of liquids.—X-ray spectra show (p. 274) that liquid molecules are arranged in a quasi-crystalline structure, but can also move about to some extent. They may link together by coordination if the molecules contain donor atoms, *e.g.* O in H_2O, and there is also some evidence that liquid molecules may sometimes have higher molecular weights than the vapour molecules, in which case the liquid is said to be *associated.* In *normal liquids* the molecular weights are the same as in the vapours.

The product $\sigma[V]^{\frac{2}{3}}$ where σ = surface tension, V = molecular volume = $\mathbf{M}/D$ (D = density) is proportional to the surface energy of 1 mol of liquid in the form of a sphere, and was called by Eötvös (1886) and by Ramsay and Shields (1893) the **molecular surface energy.** This decreases with temperature $t°$ C. according to the equation :

$$\sigma[V]^{\frac{2}{3}} = k(t_c - t - 6),$$

where k is a constant and t_c is the critical temperature. For most liquids k is approximately 2·12, but in some cases, as with water, alcohol, and acetic acid, it is smaller.

For bromine, $\sigma = 44$ at 13° C., $t_c = 302{\cdot}2$; $\mathbf{M} = 160(Br_2)$, $D = 3{\cdot}12$;

$$\therefore\ k = 44 \times \left(\frac{160}{3{\cdot}12}\right)^{\frac{2}{3}} \div (302{\cdot}2 - 13 - 6) = 2{\cdot}145.$$

Since this is very nearly 2·12, bromine is assumed to be normal.

For water, $\sigma = 73$ at 15° C., $t_c = 370$, $\mathbf{M} = 18$, $D = 1$, hence

$$k = 73 \times (18)^{\frac{2}{3}} \div (370 - 15 - 6) = 1{\cdot}437.$$

This is smaller than the normal value, 2·12. If we assume the molecular weight of water to be $x \times 18$, where x = **degree of association**, we may expect to get the normal value of k (since $18x$ is the true molecular weight), hence by division :

$$x^{\frac{2}{3}} = 2{\cdot}12/1{\cdot}437 ; \quad \therefore \ x = 1{\cdot}79.$$

This result indicates that liquid water is associated. In some cases (*e.g.* fused metals) the method leads to values of x smaller than 1, which are difficult to interpret, and the value of k has been found to vary appreciably from 2·12 for normal substances, so that the *quantitative* calculation of x is unjustified.

Another method which indicates association is the value of the **Trouton coefficient,** L_e/T_o, where L_e is the latent heat of evaporation per mol and T_o the boiling point abs. For normal liquids this is about 21, for associated liquids it is larger, *e.g.* 26·9 for alcohol and 25·9 for water.

The parachor.—MacLeod (1923) showed that the expression

$$P = \mathbf{M}\sigma^{\frac{1}{4}}/(D - d) \sim \mathbf{M}\sigma^{\frac{1}{4}}/D = V\sigma^{\frac{1}{4}},$$

where $\mathbf{M}$ = mol. wt., V = mol. vol., σ = surface tension, D = density of liquid, d = density of vapour (usually negligible in comparison with D), is practically independent of temperature for non-associated liquids almost to the critical point. Thus the values of P (called by Sugden the *parachor*) are in the ratio of the molecular volumes at temperatures for which the surface tensions are equal. Sugden found that P for a molecule is the sum of terms representing the atomic parachors and of terms characteristic of double and triple bonds, and of rings of atoms, so that the structures of molecules might be surmised from a comparison of observed and calculated parachors. The method is, however, less useful than was at first supposed. It points, for example, to cyclic structures for esters of hydrazoic acid, whereas the azide group $-N_3$ is linear (p. 560).

Solution.—When a gas is in equilibrium with a liquid solution the concentration of dissolved gas is in a fixed ratio to that in the gas-space, as required by Henry's law (p. 56). In the equilibrium state the same number of gas molecules enter and leave the liquid in unit time.

The mass of gas impinging on the liquid surface per second is $\frac{1}{4}D\bar{u}$ (p. 28) $= \frac{1}{4}D \times \frac{1}{2}\bar{c} = D\sqrt{\overline{c^2}}/\sqrt{6\pi} = 0{\cdot}230D\sqrt{\overline{c^2}}$. In oxygen at S.T.P., $D = 0{\cdot}001429$ g. per c.c., $\sqrt{\overline{c^2}} = 4{\cdot}61 \times 10^4$ cm. per sec., $\therefore$ the mass of oxygen striking 1 sq. cm. of liquid surface per second is $0{\cdot}230 \times 0{\cdot}001429 \times 4{\cdot}61 \times 10^4$ g. $= 15{\cdot}15$ g. This contains $15{\cdot}15/32 \times 1{\cdot}69 \times 10^{-24} = 2{\cdot}80 \times 10^{23}$ molecules, or the number in about 10 litres.

When the gas pressure is raised, the number of molecules per c.c. and the number striking the surface increase in the same ratio. The number of molecules per c.c. in the liquid is also increased. Hence more molecules leave the liquid than previously. At equilibrium, the same number again leave as enter per second, but if the number entering is increased n times the number per c.c. of liquid also increases n times. This corresponds with Henry's law.

If people walk into a room through one door and out through another so that as many enter as leave, then if they enter twice as fast there will be double the number in the room, although they are also leaving it at twice the previous rate.

Ultramicroscopic investigations (Traube and von Behren, 1928) show that, in dissolving, a crystal is often resolved into small aggregates of molecules, **submicrons**, which then disperse as molecules or ions after a very short interval.

Attempts have been made to find the radii of particles in solution by assuming them to be spheres and applying **Stokes's law** :

$$v = 1/6\pi\eta r,$$

where v is the mobility (=speed under unit force on the particle) and η is the viscosity of the liquid. The force acting on the particle may be osmotic pressure in diffusion, or an electric potential gradient for a migrating ion, or both combined, as in the diffusion of ions. This method gives accurate results only for large (colloidal) particles.

Polar and non-polar liquids.—Liquids may be divided into two groups : (i) **normal** or **non-polar** and (ii) **abnormal** or **polar.**

Polar liquids generally show abnormal properties :

(1) They are usually *associated* (*e.g.* water, p. 44) to more complex molecules.

(2) They have abnormally *high boiling points*. Thus in the series HF(+19·4°), HCl(−85°), HBr(−69°) and HI(−35·5°), hydrofluoric acid is abnormal and is probably associated (p. 769), and the same applies to water in the series H_2O(100°), H_2S(−61°), H_2Se(−42°) and H_2Te(−1·8°).

(3) They have *high dielectric constants* (water 81, cf. benzene 2·29).

(4) They are *good ionising solvents.*

(5) The *miscibility* of members of the same group is high (benzene, toluene ; or water, sulphuric acid), that of members of different groups is low.

(6) The *properties of mixtures are approximately additive* (density, refractive index, vapour pressure, etc.) for non-polar liquids, but those of mixtures of polar liquids are non-additive and deviate considerably from the mixture rule. This applies particularly to the *vapour pressure and boiling point curves* (p. 59).

(7) Polar liquids have usually an appreciable *heat of admixture*, non-polar liquids little or none.

Ions in solution attract dipoles in solvent molecules, which then form a sheath around each ion with the oppositely charged end of the molecule pointing towards the ion.

The effect of a solvent on ionisation was connected by J. J. Thomson and by Nernst with the **dielectric constant.** The force between two charges at a distance d in a medium of dielectric constant D is e_1e_2/Dd^2, so that the attraction tending to bind two ions together is weaker the higher the value of D. Water, hydrocyanic acid, hydrofluoric acid and acetonitrile (CH_3CN) are good ionising solvents ; alcohols are medium ionising solvents, and benzene is a poor ionising solvent, as would be expected from the values of D given below :

HCN	116	Ethyl alcohol	26
Water	81	Ammonia (liq.)	23
CH_3CN	39	Sulphur dioxide (liq.)	13·75
Methyl alcohol	35	Benzene	2·29

The ionising power of a solvent is also affected by the *chemical* properties of the solvent and solute. Solvents have been divided into (i) *levelling solvents*, such as water, in which most salts are largely and pract cally equally ionised; and (ii) *differentiating solvents*, such as acetonitrile, acetone and nitromethane, in which salts ionise to very different extents.

Solvents of type (i) mostly contain a hydroxyl group, $:\ddot{O}:H$, which Hartley (1930) suggests may have both electron-donating (due to O) and electron-accepting (due to H) properties, so that it can form covalent links with both a cation and an anion, and so prevent them from coming close enough to form an ion-pair by association.

Solvents of type (ii) are mostly electron-donating and coordinate only with cations. In this case the solvated cation and the unsolvated anion may approach close enough to associate. LiCl and NaCNS are largely dissociated in methyl alcohol (type (i), dielectric constant 30·3), but only slightly ionised in acetonitrile (type (ii), dielectric constant 36). The proton H^+ formed by the ionisation of acids in water coordinates with a water molecule to form the hydroxonium ion H_3O^+, commonly called the " hydrogen ion " ·

$$:\ddot{O}(H):+H^+Cl^- = \left[H:\ddot{O}(H)\right]^+ + Cl^-.$$

Avogadro's Number

During the nineteenth century the atomic theory and the kinetic theory of gases, although extremely useful in the development of chemistry, remained hypothetical and no convincing demonstration of the reality of atoms and molecules was possible. Some chemists (*e.g.* Ostwald) doubted their existence. From about 1900 new lines of investigation, especially in the field of radioactivity, brought such convincing proofs of the *atomic structure* of matter (and also of electricity) that this lost its hypothetical character, and the existence of atoms and electrons is now regarded as experimentally established. The sizes and masses of atoms and the sizes and shapes of molecules are now studied experimentally, and some of the results have a high order of accuracy.

When the number **N** of particles which compose 1 gm. mol. or mol of any substance is known, the mass m of the individual particle can be calculated from the molecular weight **M**:

$$m\mathbf{N} = \mathbf{M}.$$

N, Avogadro's number, has been experimentally determined in a variety of ways, all giving results in excellent agreement.

In 1933 (Virgo, *Science Progress*, 1933, **27**, 634) over twenty methods were summarised and others have since been discovered, so that only the most important can be mentioned. The table below gives the *modern* results, and the names of the investigators who *first* used the methods.

Method	$N \times 10^{-23}$
1. *Kinetic theory of gases* (Loschmidt, 1865)	5·95–6·8
2. *Brownian movement*:	
(*a*) Height distribution of particles (Perrin, 1909)	6·09
(*b*) Path of particles (Einstein, 1905; Svedberg, 1912)	6·08 ±0·01
3. *Surface tension* of solutions (de Noüy, 1924)	6·004 ±0·009
4. *Scattering of light by gases* (Lord Rayleigh, 1899)	6·03 ±0·07
5. *Law of heat radiation* (Planck, 1900)	6·03 ±0·05
6. *Charge of electron*:	
(*a*) Cloud method (Townsend, 1897)	8·3
(*b*) Suspended drop method (Millikan, 1910)	6·031 ±0·006
7. *Counting α-particles* (Rutherford and Geiger, 1908; Regener, 1908)	6·04–6·14
8. *Fine-structure of spectrum lines* (Sommerfeld, 1916)	6·08
9. *Crystal structure* (Compton, 1922)	6·022 ±0·003

Determination of the electronic charge.—Some of the values depend on the determination of the *charge on the electron*, **e**, since if **F** is the charge (1 faraday = 96,489 coulombs) on 1 g. equiv. of an ion in electrolysis:

$$\mathbf{Ne = F.}$$

The modern value of **e** is $4{\cdot}796 \times 10^{-10}$ electrostatic units or about $1{\cdot}6 \times 10^{-19}$ coulombs (Millikan, *Ann. Physik*, 1938, **32**, 34, 520). It was determined by R. A. Millikan in 1912 by the following very direct method.

Two metal plates 16 mm. apart were charged positively and negatively, respectively, by attaching them to the poles of a battery. Into the air above the plates a fine dust of pulverised oil was blown by a spray. The oil drops, which settled very slowly on account of their small size, were electrically charged by ionising the air with X-rays. A single drop fell through an aperture in the upper plate into the space between the plates, and was focused in the field of a microscope with a scale in the eyepiece, as shown *diagrammatically* in Fig. 23. By varying the potential difference between the plates, the charged drop could be made to move upwards or downwards with any desired velocity, or kept suspended. From the ratio of the velocities with and without the potential difference, the charge on the drop could be calculated.

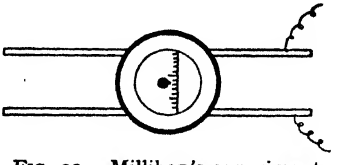


FIG. 23.—Millikan's experiment.

It was found that this charge was not constant. The variations were not continuous. Each sudden change was assumed to correspond with the gain or loss of one or more electrons by the drop, and it was found that the charge varied in small multiples of $1{\cdot}6 \times 10^{-19}$ coulombs, which is the (negative) electronic charge.

Counting alpha-particles.—Another method of finding **N** is to count the number n of α-particles emitted in a given time by a radioactive preparation and to measure the volume V c.c. at S.T.P. of helium formed in the same time from the α-particles (p. 197). Then n/V gives the number of molecules per c.c.

of gas at S.T.P., and 22,415 times this (no. of c.c. per mol) is **N**. Two methods have been used :

(1) Rutherford and Geiger, and Regener, counted the α-particles by the *scintillation method* (p. 195) and found $\mathbf{N} = 6{\cdot}05 \times 10^{23}$.

(2) In a second method used by Rutherford and Geiger (*Proc. Roy. Soc.*, 1908, **81**, 141) a long glass " firing tube " AA' (450 cm. long and 2·5 cm. wide) (Fig. 24) was exhausted, and at the end A was placed a preparation of radium

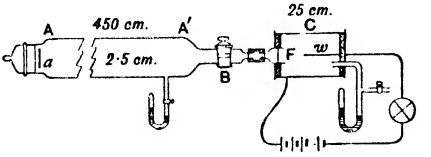


FIG. 24.—Rutherford and Geiger's apparatus.

on a lead plate a, which emitted α-particles. Some of these passed through the narrow tube into the brass ionisation chamber C, containing a gas at low pressure. A mica window at F shut off the gas from the evacuated tube AA'. Running through C and insulated from it by the ebonite ends was a metal wire w, connected through a battery and electrometer to the outer surface of the brass vessel. As each α-particle entered the ionisation chamber (at the rate of about one every second), the impact of the α-particle on the gas molecules liberated electrons from them, formed gaseous ions, and made the gas conducting, so that the electrometer gave a deflection. In this way the individual α-particles were counted, and $\mathbf{N} = 6{\cdot}14 \times 10^{23}$ was found.

The most probable value of **N** is given by Millikan (*loc. cit.*) as

$$(6{\cdot}031 \pm 0{\cdot}006) \times 10^{23}.$$

This corresponds with $2{\cdot}69 \times 10^{19}$ molecules per c.c. of gas at S.T.P. The gas constant per molecule (**Boltzmann's constant**) **k** is the gas constant per mol (p. 29) divided by Avogadro's number :

$$\mathbf{k} = \mathbf{R}/\mathbf{N} = 8{\cdot}32 \times 10^{7}/6{\cdot}03 \times 10^{23} = 1{\cdot}38 \times 10^{-16} \text{ erg/1° C.}$$

The mass of the hydrogen atom is $1{\cdot}008/\mathbf{N} = 1{\cdot}008/6{\cdot}03 \times 10^{23} = 1{\cdot}67 \times 10^{-24}$ g. ; that of any other atom of atomic weight A is $(1{\cdot}67 \times 10^{-24})A$ g.

The Brownian movement.—The particles in an aqueous suspension of gamboge are seen under the microscope to be moving erratically in zig-zag paths. This is the *Brownian movement*, discovered in pollen suspensions by Robert Brown in 1827, and shown by all fine suspended particles. It was explained by Wiener in 1863 as due to the unequal bombardment on different sides of the suspended particle by the moving molecules of the liquid, this jostling the particle in various directions. Svedberg in 1906 found that the average path agrees with that calculated by Einstein in 1905 from the kinetic theory.

Perrin (*Atoms*, 1923, Chaps. 3–4) found microscopically that the distribution of gamboge particles in a suspension varies with the height (Fig. 25) ;

near the surface a rise of $\frac{1}{20}$ mm. halved the number per c.c. This resembles the fall of atmospheric pressure with height according to the logarithmic barometer formula. Both the gamboge particles and the air molecules are supported against gravity by their kinetic energies.

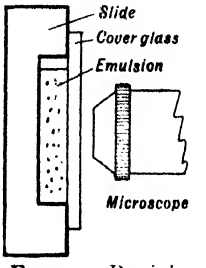


FIG. 25.—Perrin's experiment.

If n and n' are the numbers of particles per c.c. at two heights h cm. apart and if the suspension obeys the "gas" laws, the osmotic pressures p and p' are in the ratio of n and n' and the formula shows that h for $n'/n = \frac{1}{2}$, *i.e.* the height in which the pressure or density is halved, is inversely proportional to the molecular weight of the particles. To halve the pressure in oxygen, h is 5 kilometres, in hydrogen $5 \times 32/2 = 80$ km., in carbon dioxide $5 \times 32/44 = 3{\cdot}64$ km., and in the gamboge suspension a small fraction of a mm., from which the "molecular weight" could be calculated. Since the gamboge particles can be counted and the mass per c.c. found by evaporation and weighing, the number of particles per g. mol. could be found. This was found to be $6{\cdot}8 \times 10^{23}$, which is very near the other values of Avogadro's number. From the Brownian movement of the particles in tobacco-smoke, de Broglie calculated Avogadro's number as $6{\cdot}43 \times 10^{23}$.

CHAPTER III

THE PHASE RULE AND SOLUTIONS

The Phase Rule

Degrees of freedom.—The volume of a gas depends on temperature and pressure, but if any two of these variables (pressure, volume and temperature) are fixed the third has a definite value. The volume of a liquid or solid is also fixed at a given temperature and pressure. It is most convenient to consider specific volume (1/density), and the state of any homogeneous phase (gas, liquid or solid) of a pure substance is determined when any *two* of the variables—pressure, temperature and specific volume—are fixed. *A pure substance in one phase* ($P=1$) *has two degrees of freedom* ($F=2$). *The number of degrees of freedom is the smallest number of independent variables required to define the state of equilibrium of the system completely.*

A pure liquid is in equilibrium with its vapour at a given temperature at a definite pressure (the vapour pressure), and the liquid and vapour phases are completely determined. If the volume is decreased some vapour condenses; if the volume is increased some liquid evaporates, but in each case the original pressure is restored when the system comes to equilibrium. A mixture of ice and water behaves similarly, ice melting or water freezing as the volume is decreased or increased. *A system of two phases* ($P=2$) *of a pure substance has one degree of freedom* ($F=1$).

Ice, water and water vapour coexist at one temperature and one pressure only: $+0.0077^\circ$ and 4·57 mm., the *triple point* for water. *A system of three phases* ($P=3$) *of a pure substance has no degree of freedom* ($F=0$).

A little common salt passed into a barometer tube containing water and water vapour dissolves in the water, and the vapour pressure decreases. *A system of two phases* ($P=2$), *e.g.* solution and vapour, *of two components* ($C=2$) *has two degrees of freedom* ($F=2$) instead of only one with a pure substance ($C=1$), since the vapour pressure now depends on the concentration of the dissolved substance, which is an extra variable. When the solution is saturated with salt an extra phase (solid salt) appears ($P=3$) and the pressure is now constant: the appearance of another phase reduces the number of degrees of freedom by one ($F=1$), the pressure now depending only on a single variable, the temperature.

The concentration of a *saturated* solution of salt, *when no water vapour is present* ($P=2$), depends both on temperature and pressure ($F=2$), but if the solution is in equilibrium with vapour as well as solid salt it depends only on temperature ($F=1$), since an additional phase appears ($P=3$).

Components.—A system of phases is formed from a certain number of substances or *components*, some or all of which may be present in every phase. Systems containing ice, water and water vapour contain only one substance; those containing salt, salt solution and water vapour contain two (salt and

water). The **number of components** C is *the least number of substances from which every phase in a system can be formed.*

For the equilibrium $CaCO_3 \rightleftharpoons CaO + CO_2$ the number of components is 2, *e.g.* CaO and CO_2, forming two of the phases, from which the third phase $CaCO_3$ may be composed. We might choose CaO and $CaCO_3$, when $CO_2 = CaCO_3 - CaO$, or $CaCO_3$ and CO_2, when $CaO = CaCO_3 - CO_2$, but the number of components is always 2.

The phase rule.—Consider the following table, which summarises results just described:

C	P	F	Equilibria
1	2	1	Water (liq.) $\rightleftharpoons$ Water (vap.)
1	2	1	Water (solid) $\rightleftharpoons$ Water (vap.)
1	2	1	Water (solid) $\rightleftharpoons$ Water (liq.)
1	3	0	Water (solid) $\rightleftharpoons$ Water (liq.) $\rightleftharpoons$ Water (vap.)
2	2	2	Salt (dissd.) $\rightleftharpoons$ Salt (solid)
2	2	2	Water (in sol.) $\rightleftharpoons$ Water (vap.)
2	3	1	Water (in sol.) $\rightleftharpoons$ Water (vap.) Salt (dissd.) $\rightleftharpoons$ Salt (solid)

In all cases a simple relation exists between the number of phases P, the number of components C, and the number of degrees of freedom F, viz.:

Number of phases + Number of degrees of freedom = Number of components + 2

$$P + F = C + 2.$$

This applies to all heterogeneous systems in equilibrium and is called the **phase rule** (Willard Gibbs, 1876).

Besides the above examples we may consider two other cases.

(i) *A gas in contact with its saturated solution.* Here $P = 2$ and $C = 2$, hence $F = C + 2 - P = 2$. The concentration of the solution (solubility of the gas) therefore depends on pressure and temperature.

(ii) *Two partly miscible liquids, e.g.* ether and water. If vapour is present, $P = 3$ (2 liquid layers + vapour), $C = 2$; $\therefore F = C + 2 - P = 1$, *i.e.* the composition of each layer depends only on temperature.

One Component Systems

Water.—The equilibria between the *phases of water* are shown *diagrammatically* in Fig. 26. AL is the vapour pressure curve of liquid water, ending at the critical point L. Since increase of pressure at a given temperature condenses vapour to liquid, the liquid and vapour fields are as shown. SA is the vapour pressure curve of ice; it has a greater slope (exaggerated in the figure) at the triple point than that of water, AL. A is the triple point, where ice, water and vapour are in equilibrium. AB is the melting curve of ice at different pressures;

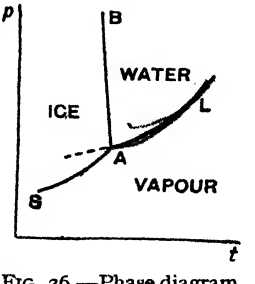


FIG. 26.—Phase diagram for water.

since the m.p. is lowered by increase of pressure, AB slopes to the left. The dotted curve represents supercooled water, which is a *metastable state*, since in presence of ice the liquid would solidify. The vapour pressures of metastable states are always greater than those of stable states at equal temperatures.

For carbon dioxide the point A lies at about 5 atm. pressure, so that under atmospheric pressure solid carbon dioxide (" dry ice ") passes directly into gas without melting. The liquid is contained in cylinders under pressure, but when released through a valve it at once solidifies.

At higher pressures several different *forms of ice* appear, so that the upper part of the curve AB is complicated. In Fig. 27 SA is the vapour pressure curve of ordinary ice, AL that of liquid water, and AB gives the effect of pressure on the melting point of ice I. At a pressure of 2115 kg./sq. cm. there is a break at B and ice III appears, the melting point of which *increases* with rise of pressure. B (−22°) is the triple point of ice I, ice III and water. Above 2500 kg./sq. cm. ice III forms from liquid water, below this pressure ice I forms even in the ice III region. If at B a small increase of pressure is applied, corresponding to a fall in temperature, the system moves along BD, representing equilibrium between ice I and ice III. At D a new triple point appears with the three solid phases ice I, ice II and ice III. On slightly reducing the pressure and lowering the temperature the ice III disappears and the system moves along a line DE representing equilibrium between ice I and ice II. Owing to the slow rate of transformation of ice III it is possible to move along BD beyond D into a region of metastable equilibrium between ice I and ice III.

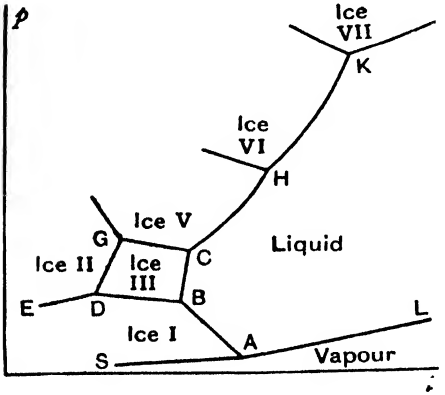


FIG. 27.—Forms of ice.

If the temperature and pressure at D are both raised instead of lowered the system passes along DG, representing the equilibrium between ice II and ice III. At G ice V appears and this is a triple point with ice II, ice III and ice V in equilibrium. On raising the temperature with a slight decrease of pressure the system reaches the triple point C, which can also be reached from B by a large rise in pressure and a small rise in temperature. At C liquid, ice III and ice V are in equilibrium. Increase in pressure and temperature leads along CH to the triple point H (0·16°) of liquid, ice V and ice VI. Further increase in temperature and pressure results in the disappearance of ice V, and along HK liquid and ice VI are in equilibrium. At still higher pressures ice VII appears at K. It will be seen that ice II is surrounded by solid phases and it can never be in equilibrium with liquid water.

The densities of all the forms, except ice I, are greater than 1 : ice II 1·03, ice III 1·04, ice V 1·09, ice VI 1·06. Ice VI is stable only above 0° and can exist at 80°. These forms of ice were discovered by Tammann and by Bridgman.

Sulphur.—Each *allotropic form* of a substance which can exist in equilibrium with vapour has its own vapour pressure curve. This is shown in Fig. 28 for the two common allotropic forms of sulphur, rhombic or α-sulphur and monoclinic or β-sulphur.

OP is the vapour pressure curve of α-sulphur, ending at *P*, which is a *transition point* (96°) above which β-sulphur is stable. At the transition point the two forms are in equilibrium: $S_\alpha \rightleftharpoons S_\beta$. The change takes place only slowly, so that α-S can exist in a metastable state at temperatures above 96° for some time, this being shown by *PR*.

PQ is the vapour pressure curve of β-sulphur; it ends at *Q* which is the melting point (120°) of β-S, and *QZ* is the vapour pressure curve of liquid sulphur. *QR* represents supercooled liquid sulphur, *QS* the effect of pressure on the melting point of β-S, which is increased by raising the pressure.

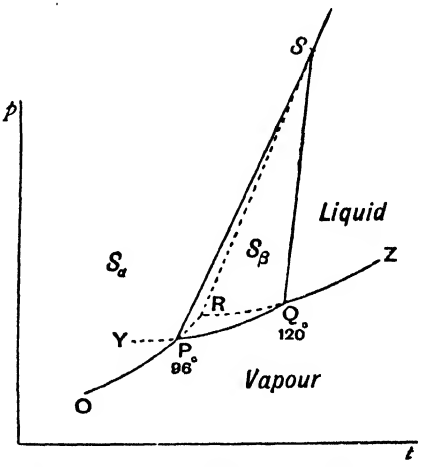


FIG. 28.—Phase diagram for sulphur.

PS gives the effect of pressure on the transition temperature of α- and β-sulphur, which increases with pressure. It meets *QS* at *S* (151° and 1288 atm.; the diagram is not drawn to scale).

Since *PR* represents metastable α-S and *QR* metastable liquid sulphur, *R* is the metastable melting point of α-S, 112·8°. The effect of pressure on this is shown by *RS*. *PY* is the vapour pressure curve of metastable β-S, which can exist for a time after crystallising from liquid sulphur, but passes fairly quickly below 96° into the stable α-S.

A more complicated system is that of *phosphorus*, described on p. 595.

TWO COMPONENT SYSTEMS

In systems of two components the maximum number of phases (when $F=0$) is four, since $P=C+2-F=2+2-0=4$. The phases may be solids, liquids or a gas, and either pure substances or solutions, *e.g.*:

I. *Two pure solids and one gas*: *dissociation* of hydrated salts, calcium carbonate, or barium peroxide.

II. *Solutions of gases in gases* ("mixed" gases): a mixture of gases can form only one phase.

III. *Solutions of gases in liquids.*

IV. *Solutions of liquids in liquids.*

V. *Solutions of solids in liquids* (the most important case).

VI. *Solutions of solids in solids* (solid solutions).

Dissociation.—Some crystal hydrates lose water and fall to powder, or *effloresce*, on exposure to air. The pressure of water vapour over the salt can be measured by passing a crystal of the salt above the mercury in a barometer tube: the pressure is constant at a given temperature and increases with the temperature. This shows that there is one degree of freedom ($F = 1$), and as there are two components ($C = 2$) the number of phases is $P = 2 + 2 - 1 = 3$, *i.e.* water vapour and *two* solids. The pressure is independent of the amounts of the phases. One solid is the original salt, the other is the product of its dehydration, either a lower hydrate: $CuSO_4, 5H_2O \rightleftharpoons CuSO_4, 3H_2O + 2H_2O$ (vap.), or the anhydrous salt: $Na_2SO_4, 10H_2O \rightleftharpoons Na_2SO_4 + 10H_2O$ (vap.).

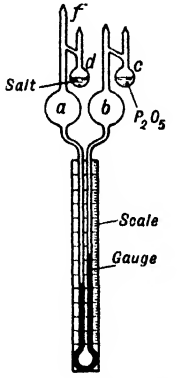


FIG. 29.—Tensimeter.

When the dissociation pressure at room temperature exceeds the pressure of water vapour in the atmosphere the salt loses water and effloresces, but if the two pressures are about the same the hydrate is stable. The pressure of atmospheric water vapour, about $\frac{2}{3}$ the saturation pressure, is about 15 mm. at 25°. If the dissociation pressure over the hydrate is very small, the solid may absorb moisture from the air and liquefy or *deliquesce* (p. 73).

The dissociation pressure of a salt hydrate is measured in a *tensimeter* (Fig. 29).

The powdered salt is put in the bulb *d* and P_2O_5 in *c* and the necks sealed. The gauge contains olive oil or bromnaphthalene. The apparatus is laid on its side so that the liquid runs into *a* and *b*, and the air is pumped out through *f*, which is then sealed. The tensimeter is supported in a vertical position in a thermostat, and when the pressure is constant (usually after several hours) it is read off on a millimetre scale behind the gauge.

If a salt forms several hydrates, such as copper sulphate, the powder is exposed in a desiccator over P_2O_5 and the dissociation pressure measured from time to time in a tensimeter. Each hydrate has its own dissociation pressure.

The first pressure corresponds with the dissociation:

$$CuSO_4, 5H_2O \rightleftharpoons CuSO_4, 3H_2O + 2H_2O \text{ (vap.)},$$

and is constant along *AB* (Fig. 30) so long as the *two* solid hydrates (5 and 3) are present. When all the 5-hydrate disappears and only $CuSO_4, 3H_2O$ and $CuSO_4, H_2O$ are present, the pressure drops sharply to a lower value, and is again constant along *CD* until only $CuSO_4, H_2O$ and $CuSO_4$ are present, when it drops to the value along *EF*. By analysing the solid when drops of pressure occur the compositions of the hydrates can be found.

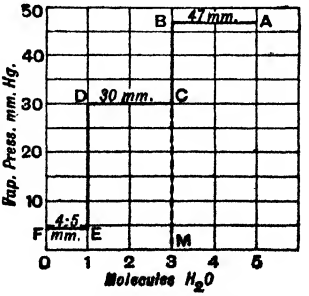


FIG. 30.—Vapour pressure curves for hydrates at 50°.

Solutions

Mixed gases.—When gases which do not react chemically are mixed in a vessel the pressure is given by **Dalton's law of partial pressures** (1801): *the pressure is the sum of the pressures* (partial pressures) *each component would exert if it alone occupied the whole volume of the mixture, at the same temperature.*

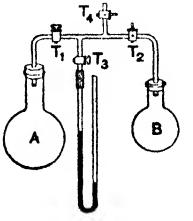


FIG. 31.—Experiment on partial pressures.

EXPT. 1.—Connect two flasks by tubes with a manometer (Fig. 31). A contains air and B carbon dioxide. Close T_2 and T_3 and partly evacuate A through T_4 with a water pump. Close T_4 and connect A and B in turn with the manometer by means of T_1, T_2 and T_3. Subtract the readings from the barometer reading. Let the gas pressures be p_A and p_B. Open T_1 and T_2 and let the gases mix. Read the final pressure p as before.

The total volume is $v_A + v_B$ and the *partial pressures* are, by Boyle's law: $p_A v_A/(v_A + v_B)$ and $p_B v_B/(v_A + v_B)$. Show that the sum of these is equal to p.

If p_1 and p_2 are the partial pressures and p the total pressure:

$$p = p_1 + p_2. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Let v_1 and v_2 be the volumes of the separate gases under the *total* pressure p. Then if v is the volume of the mixture:

$$pv_1 = p_1 v \quad \text{and} \quad pv_2 = p_2 v;$$

$$\therefore \; v_1/v_2 = p_1/p_2. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

In the case of *a moist gas collected over water*, if p_2 = vapour pressure of water, then the pressure of the *dry* gas is $p - p_2$.

Solutions of gases in liquids.—The *solubility* of a gas in a liquid may be measured by an **absorptiometer** (Fig. 32). The gas is measured over mercury in the burette A and the volume reduced to S.T.P. Some gas is passed into the absorption vessel C, the volume of liquid, *e.g.* water previously boiled to expel dissolved air, remaining being the original volume minus the volume run out. A and C are connected by a flexible lead or copper tube. The gas is shaken with the liquid until the solution is saturated. The vessel C is placed in a bath of water at a constant temperature and the pressure adjusted by the levelling tube B. The contraction is read off on the burette, and corrected for the vapour pressure of the liquid, temperature and barometric pressure. Bunsen's **absorption coefficient** β is the volume of gas *reduced to S.T.P.* which saturates 1 volume of solvent at a given temperature under a gas partial pressure of 1 atm.

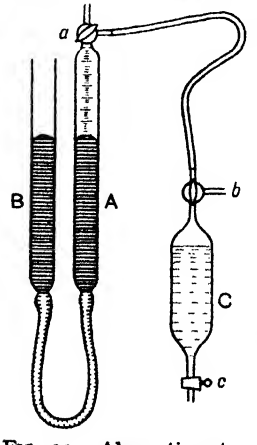


FIG. 32.—Absorptiometer.

If the gas is very soluble (*e.g.* ammonia, hydrochloric acid) it is bubbled in a bulb-tube through a

weighed volume of water until the latter is saturated. The amount of gas dissolved is then found by weighing or by chemical analysis (*e.g.* titration).

The amount of gas dissolved by a fixed volume of liquid depends on (1) the chemical composition of the gas and of the liquid, (2) the temperature, (3) the pressure. The effect of pressure is given by **Henry's law** (1803): *the mass of gas absorbed by a fixed volume of liquid at a given temperature is proportional to the pressure.*

Since the volume of a given amount of gas is inversely proportional to the pressure (Boyle's law), *a given volume of liquid absorbs the same volume of gas at all pressures.* Ostwald's **solubility coefficient** α is the volume of gas dissolved by 1 vol. of liquid under the conditions of experiment. Hence $\alpha = \beta(1 + 0{\cdot}00367t)$, where t = temp. C.

Solubility of a mixture of gases in a liquid.—*The amount of one gas dissolved from a mixture of gases is proportional to its partial pressure when the gas is in equilibrium with the liquid.* This is **Dalton's extension** (1807) **of Henry's law.**

EXAMPLE.—The absorption coefficients of nitrogen, oxygen and argon in water at 0°, and the percentages by volume of these gases in dry air free from carbon dioxide, are given below.

Gas.	*Percentage by vol.*	*Partial pressure (total = 1 atm.).*	*Absorption coefficient.*
Nitrogen	78	0·78	0·0239
Oxygen	21	0·21	0·0489
Argon	1	0·01	0·053

By multiplying partial pressure by absorption coefficient the volume of each gas dissolved in 1 vol. of water saturated with a large volume of air (constant composition) is found:

nitrogen, 0·01864; oxygen, 0·01027; argon, 0·00053; sum, 0·02944.

The gas expelled by boiling has this composition, or contains in p.c. by vol.:

$$\text{nitrogen } \frac{1{\cdot}864}{0{\cdot}02944} = 63{\cdot}3\,; \quad \text{oxygen } \frac{1{\cdot}027}{0{\cdot}02944} = 34{\cdot}9\,; \quad \text{argon } \frac{0{\cdot}053}{0{\cdot}02944} = 1{\cdot}8.$$

The proportions of oxygen and argon have increased, since these are more soluble than nitrogen. By shaking water with an excess of this gas, the dissolved part when expelled by boiling will be still further enriched in oxygen. After 8 repetitions the gas contains over 90 p.c. of oxygen. (*Mallet's process* for enriching air in oxygen.)

If the partial pressure of a gas above its solution can be reduced to zero all the dissolved gas is expelled. This can usually be done by (i) reducing the pressure by an air-pump, (ii) passing a stream of indifferent gas through the solution, (iii) boiling the solution, when the gas passes off with the steam. When the gas and solvent evaporate together to form a vapour of the same composition as the liquid (see p. 60) no separation is possible.

Henry's law does not apply to very soluble gases, nor accurately to carbon dioxide. It does not apply to hydrogen chloride, or ammonia at room tempera-

ture, in water, but at 100° the solubility of ammonia (which is then quite small) follows the law. At pressures above 2 atm. deviations occur with more soluble gases, but less soluble gases obey the law up to about 10 atm.

The Bunsen's absorption coefficients given in the table are the volumes at S.T.P. absorbed by 1 vol. of water at the given temperature under a pressure of 760 mm. of *dry* gas, except for HCl, for which the total pressure of gas and water vapour is 760 mm.

Gas	0°	10°	15°	20°	30°	40°	50°	60°
NH_3 -	1300	910	802	710	—	—	—	—
HCl -	506	474	458	442	411	386	362	339
CO_2 -	1·713	1·194	1·019	0·878	0·665	0·53	0·44	0·36
O_2 - -	0·049	0·038	0·034	0·031	0·026	0·023	0·021	0·0195
N_2 -	0·0239	0·0196	0·0179	0·0164	0·0138	0·0118	0·0106	0·0100
H_2 -	0·0215	0·0198	0·0190	0·0184	0·0170	0·0164	0·0161	0·0160

Gases are usually less soluble in salt solutions than in pure water, hence chlorine and carbon dioxide may be collected over saturated brine without much loss.

Solutions of liquids in liquids.—Some liquids, such as water and mercury, are practically (probably not absolutely) *immiscible*; others, such as ether and water, are *partly miscible*; others, such as water and sulphuric acid, are *completely miscible.*

Water when shaken with ether becomes saturated when 100 g. of water take up 5·8 g. of ether at 22°. If more ether is added a lighter layer separates containing 4·12 g. of water to 100 g. of ether. With more ether (if the layers are shaken) the composition of each layer remains constant, but the lower (aqueous) layer gradually disappears, until finally the whole liquid has the composition of the upper layer. Further quantities of ether may now be added without any separation into layers. These results agree with the phase rule (p. 51).

The compositions of some liquid layers in equilibrium at 22° are :

	Subst. in 100 g. of water	Water in 100 g. of subst.
Ether - - - - - -	5·8 g.	4·12 g.
Chloroform - - - -	0·62 ,,	0·10 ,,
Carbon disulphide - -	0·218 ,,	10·81 ,,

Critical solution temperature.—When phenol is added to water so that more than 8 p.c. of phenol is present, two liquids are formed, one a solution of phenol in water and the other a solution of water in phenol. The same liquids are formed if water is added to phenol. They are shown as *A* and *B* in Fig. 33. Their compositions are independent of the amounts of phenol and water mixed. At higher temperatures the water layer is enriched in phenol along *AC* and the phenol layer enriched in water along *BC*, the ends of each horizontal giving

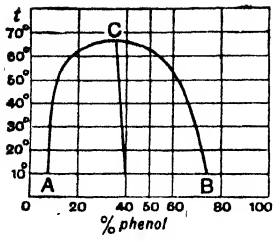


FIG. 33.—Solubility curves for phenol and water.

the compositions, until at C the two phases are identical and only one liquid is present. The temperature corresponding with C is called the *critical solution temperature.* For phenol and water this is 66°.

In some cases the miscibility decreases with rise in temperature, *e.g.* below 18° triethylamine and water mix in all proportions whilst at higher temperatures two layers separate. The curve is then like ACB inverted and the critical solution temperature is at a lower temperature. With nicotine and water both a maximum and a minimum occur and the curve is a closed oval.

The distribution law.—Iodine shaken with chloroform and water dissolves in each, but the chloroform layer (as seen from the colour) contains most of the iodine. Berthelot and Jungfleisch (1872) found that the weights of dissolved substance in unit volume of each liquid were in a constant ratio, independent of the amounts of the substance or of the liquids. *A substance is shared by two immiscible solvents in a constant ratio,* called the **distribution** (or **partition**) **ratio.**

If c_1, c_2 are the concentrations (weights per unit volume) of the solute in the two layers, then :

$$c_1/c_2 = \text{const.} = k.$$

At 25° an aqueous solution of iodine containing 0·0516 g. per litre is in equilibrium with a solution of iodine in carbon tetrachloride containing 4·412 g. per litre. The *distribution coefficient* is :

$$\frac{\text{concentration in carbon tetrachloride}}{\text{concentration in water}} = \frac{4{\cdot}412}{0{\cdot}0516} = 85{\cdot}5.$$

A saturated solution of iodine in water at 25° contains 0·340 g./lit. Hence a solution of iodine in carbon tetrachloride in equilibrium with a saturated solution in water contains $0{\cdot}340 \times 85{\cdot}5 = 29{\cdot}1$ g. of iodine per litre.

This is a three component system, hence $F = C + 2 - P = 3 + 2 - 3 = 2$, so that when three phases (2 solutions and vapour) are present the concentration of *one* solution may be varied at a given temperature but that of the other is then fixed.

Nernst (1892) showed that *the distribution ratio c_1/c_2 is constant only when the solute has the same molecular weight in each solvent.* The values for the concentrations in g./100 c.c. for benzoic acid are :

c_1 = concentration in water layer -	0·15	0·195	0·289
c_2 = " " benzene " -	2·42	4·12	9·7
c_1/c_2 - - - - - -	0·062	0·047	0·030
$c_1/\sqrt{c_2}$ - - - - - -	0·0964	0·0961	0·0928

If the acid exists in benzene mostly as double molecules $(C_6H_5COOH)_2$, a *dimeric form*, the law of mass action (see Chap. V) shows that the *small* concentration of *single* molecules in benzene is proportional to $\sqrt{c_2}$, since :

$$\text{conc. of } (C_6H_5COOH)_2 = \text{const.} \times (\text{conc. of } C_6H_5COOH)^2.$$

For the distribution of *single molecules* (there are practically no double molecules in water) between benzene and water the distribution law then gives $c_1/\sqrt{c_2} = \text{const.}$, which is seen to be approximately true.

Distillation

Fractional distillation.—The separation of a mixture of two liquids *A* and *B* by fractional distillation may be explained in terms of the **boiling-point curves.** If the liquids are *completely miscible* these are of *three types* (I, II and III,

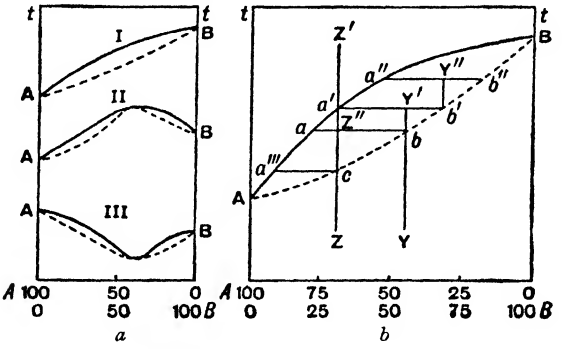


Fig. 34.—Boiling-point curves.

Fig. 34*a*). The percentages of *A* and *B* are given on the *x*-axis and the boiling points on the *y*-axis. Since the composition of the vapour usually differs from that of the liquid, two curves are needed for each mixture. The upper full curves refer to the vapour and the lower dotted curves to the liquid. Below the dotted curve all is liquid, above the full curve all is vapour, between the two curves both liquid and vapour are present, at a given pressure.

Case I: *the boiling points of all mixtures lie between those of pure A and B.*

On heating liquid represented by *Y* (Fig. 34*b*) * to the temperature *b*, vapour of composition *a* is formed, richer in *A*. Only a drop of liquid of composition *a* distils, so the temperature is allowed to rise to *Y'*, when the vapour has the composition *a'* and the liquid residue *b'*. The vapour on cooling condenses to liquid *Z*. By distilling liquid *Z* again, the distillate *a'''* is still richer in *A*, and by repeating the process nearly pure *A* may be obtained. The residue *b'* in the flask is heated to *Y''*, when a residue *b''* still richer in *B* and a distillate *a''*, which can be further distilled as before, are obtained. By repeating the process nearly pure *B* can be obtained.

* Parts of this figure are first explained in the section on solid solutions, p. 66.

In practice a **rectifying column** is used. A long vertical tube packed with glass beads or rolls of sheet metal is fitted to the distillation flask. In this column the vapour and the liquid condensed from it come into intimate contact. The column is hotter below and the liquid condensed drops back into the flask, only the lower boiling fraction passing out of the cooler top of the column to the condenser. The composition corresponding with the temperature at the top of the column may be nearly pure *A*. The temperature in the flask rises and ultimately nearly pure *B* remains.

Case II: *the boiling-point curve has a maximum*, where the compositions of liquid and vapour are the same; a mixture of this composition distils unchanged, and is called a **constant boiling mixture** or **azeotropic mixture** (Greek: *a*, not; *zeo*, I boil; *tropé*, change). It behaves like a pure substance, but (unlike that of a pure substance) its composition changes when the distillation *pressure* is altered.

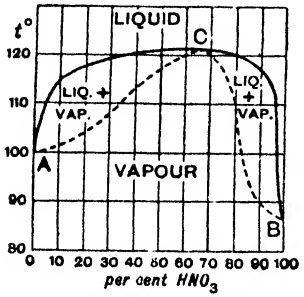


FIG. 35.—Boiling-point curves for nitric acid and water.

The boiling-point curves for mixtures of *nitric acid and water* are shown in Fig. 35. On distilling nitric acid weaker than 68·2 p.c. (the azeotropic mixture, b.p. 121°) a still weaker acid passes over and the residue approaches the composition *C*, when it distils unchanged. With acids above 68·2 p.c., more concentrated acid distils and the residue again approaches *C* (with very concentrated acids, decomposition occurs, except under reduced pressure).

Solutions of hydrofluoric (37 p.c., 120°), hydrochloric (20·22 p.c., 110°), hydrobromic (48 p.c., 126°), hydriodic (57 p.c., 127°) and sulphuric (98·3 p.c., 338°) acids also show maximum boiling points. In such cases there is probably chemical action between the solvent and solute, but the constant boiling mixture has not a definite formula and its composition changes with pressure.

Case III: *the boiling-point curve has a minimum*, where the compositions of liquid and vapour are the same. A mixture of minimum boiling point distils and the residue approaches pure *A* or pure *B* according as the mixture distilled contains more *A* or more *B* than the mixture of minimum boiling point (which would distil unchanged).

Examples of this type are mixtures of water and ethyl alcohol (4·4 p.c. H_2O, 78·15°), water and *n*-propyl alcohol (71·7 p.c. propyl alcohol, 87·7°) and benzene and ethyl alcohol (68·24°). Absolute (100 p.c.) alcohol for mixing with petrol is made from 95 p.c. alcohol (b.p. 78·5°) by adding the correct amount of benzene, when a *ternary azeotropic mixture* (74·1 p.c. benzene, 18·5 p.c. alcohol, 7·4 p.c. water, b.p. 65°) distils over, removing all the water and leaving anhydrous alcohol.

Distillation in steam.—In the purification of liquids of fairly high boiling points which are practically non-miscible with water (*e.g.* nitrobenzene, b.p. 211°; aniline, b.p. 184°) the liquid and water in a flask are heated till the

water boils and a current of steam from a can is passed through the mixture by a tube. The vapours passing over are condensed and the two liquids collected are parted by a separating funnel.

Since the liquids are practically non-miscible *the ratio of their partial pressures in the vapour is equal to the ratio of their vapour pressures at the boiling temperature of the mixture.* The ratio of the partial pressures p_1 and p_2 is (p. 55) equal to the ratio of the vapour volumes v_1 and v_2 at atmospheric pressure. By multiplying these volumes by the vapour densities D_1 and D_2 the ratio of weights w_1 and w_2 is found. The vapour densities are in the ratio of the molecular weights M_1 and M_2. Hence we find **Naumann's equation** (1877):

$$\frac{w_1}{w_2} = \frac{v_1 D_1}{v_2 D_2} = \frac{p_1}{p_2} \cdot \frac{M_1}{M_2}.$$

Liquids of *high molecular weight* (and usually high b.p.) generally distil freely in steam, as this equation shows, and this is important for their purification.

For aniline (1) and water (2): $p_1 = 49{\cdot}5$ mm., $p_2 = 760 - 49{\cdot}5 = 710{\cdot}5$ mm., $M_1 = 93$, $M_2 = 18$; $\therefore\ w_1/w_2 = 49{\cdot}5 \times 93/710{\cdot}5 \times 18 = 0{\cdot}36$. Hence the percentage of aniline in the distillate is 26·5.

Naumann's equation may be used to find (i) the vapour pressure of a liquid at the boiling point of the mixture (which is always *lower* than the boiling point of water), or (ii) the molecular weight of the liquid (when the result is not very accurate).

At 98·7° and 758·9 mm. the steam distillate from dimethylaniline contained 23·5 p.c. of this. The vapour pressure of water at 98·7° is 725·5 mm. The molecular weight of dimethylaniline is ($w_1/w_2 = 23{\cdot}5/(100 - 23{\cdot}5) = 0{\cdot}307$):

$$M_1 = 18 \times \frac{725{\cdot}5}{758{\cdot}9 - 725{\cdot}5} \times 0{\cdot}307 = 120{\cdot}1.$$

Solutions of Solids in Liquids

The most important class of solutions is that of solids in liquids. *A solution which can exist in equilibrium with excess of solid solute under given conditions* (*e.g.* at a fixed temperature) *is called a* **saturated solution.**

The **solubility** is the maximum weight in g. of solid dissolved by 100 g. of *solvent* at the given temperature *in presence of the solid salt.* For very soluble salts it is sometimes taken as the number of g. of solute in 100 g. of *solution.* For salts containing water of crystallisation, the solubility is the weight of *anhydrous* salt (salt free from water) per 100 g. of water in the saturated solution.

In a saturated solution *in the absence of the vapour phase* there are two phases; $\therefore\ F = C + 2 - P = 2 + 2 - 2 = 2$, so that the concentration (solubility) depends on both temperature and pressure. The solubility depends (1) on the chemical characters of solute and solvent, (2) on temperature, and (3) to a slight extent on pressure, in some cases (sodium chloride) increasing, in other

cases (ammonium chloride) decreasing, with increase of pressure. The solubility of small particles is somewhat higher than that of large crystals (p. 377).

The solubility usually increases with temperature. In a few cases, such as sodium chloride, it is nearly independent of temperature, and in others, such as calcium sulphate above 40°, it decreases with rise of temperature.

EXPT. 2.—Place a tube containing calcium butyrate solution saturated at the ordinary temperature in a beaker of hot water. Crystals of the salt separate. They redissolve on cooling.

Solubilities at various temperatures are represented by **solubility curves,** in which abscissae represent temperatures and ordinates solubilities (Fig. 36).

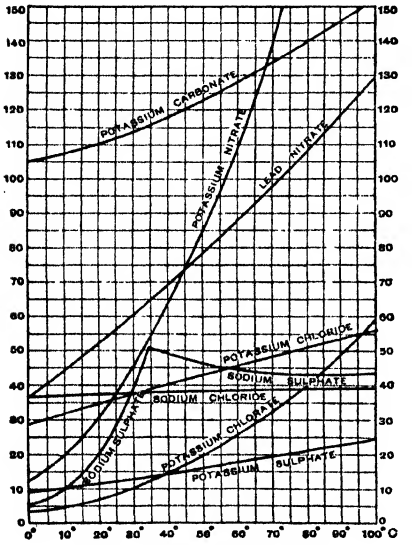


FIG. 36.—Solubility curves.

The solubility always refers to a definite *solid phase*; allotropic forms (*e.g.* rhombic and monoclinic sulphur) and different hydrates (*e.g.* $ZnSO_4,7H_2O$ and $ZnSO_4,6H_2O$) have different solubilities, except at a transition temperature, when the solids are in equilibrium. It may happen that a change of solid phase occurs on heating the solid in contact with the solution (*e.g.* $Na_2SO_4,10H_2O$ into Na_2SO_4 at 32°), in which case the solubility curve shows a break.

When a hot saturated solution is cooled in absence of solid it may remain *supersaturated*, *i.e.* it does not deposit solid and contains more solute than corresponds with the equilibrium value (in presence of solid) at a given temperature. Crystallisation occurs in presence of solid salt (or sometimes of an isomorphous salt). A supersaturated solution may crystallise spontaneously when strongly cooled (Miers and Isaac, *J.C.S.*, 1906, **89**, 413) or when exposed to shock (Young, *J.A.C.S.*, 1911, **33**, 148). Some salts (Glauber's salt, sodium thiosulphate, sodium acetate, etc.) show supersaturation much more easily than others.

EXPT. 3.—Heat on a water bath 100 g. of crystallised sodium thiosulphate ("hypo") in a conical flask with the neck plugged with cotton wool. The salt melts and forms a very concentrated solution with the water of crystallisation. On cooling this remains supersaturated. Remove the plug and drop in a crystal of "hypo". The liquid crystallises and heat is evolved, as may be shown by immersing a small bulb containing ether in the mass and lighting the ether vapour issuing from the tube attached to the bulb.

EXPT. 4.—Fuse some "hypo" crystals in a long test-tube and pour over the liquid carefully, avoiding mixing, a supersaturated solution of sodium acetate

made by warming the crystallised salt with ¼ its weight of water. Plug the tube with cotton wool and allow to cool. Remove the plug and drop in a crystal of " hypo ". This falls through the acetate solution without causing it to crystallise, but when it reaches the " hypo " solution this crystallises. Now drop in a crystal of sodium acetate: the upper liquid crystallises.

In determining solubility an excess of powdered salt is stirred with water at a constant temperature (*e.g.* in a thermostat) until the solution is saturated. The solution is allowed to settle and a portion withdrawn into a Landolt pipette (Fig. 37) by suction, the pipette is taken out, wiped, closed with pieces of glass rod and rubber tubing, cooled and weighed. The solution and crystals are then washed out of the pipette and the amount of solute determined either by evaporation in a weighed dish or by analysis (Palmer, *Experimental Physical Chemistry*, Cambridge, 1941, 65 f.; for another apparatus see King and Partington, *J.C.S.*, 1926, 20).

An approximate solubility curve can be found by the *synthesis method*. A weighed amount of finely powdered salt (*e.g.* KNO_3) is added to a known amount of water in a beaker until a little remains undissolved on stirring. The temperature is slowly raised until a mere trace of solid remains. The temperature is read. From the known weights of salt and water the solubility at that temperature is calculated. The temperature is then raised, a further weighed portion of salt is added, and the process described is repeated. In this way several points on a solubility curve are determined (Partington, *School Course of Chemistry*, 1936, 13).

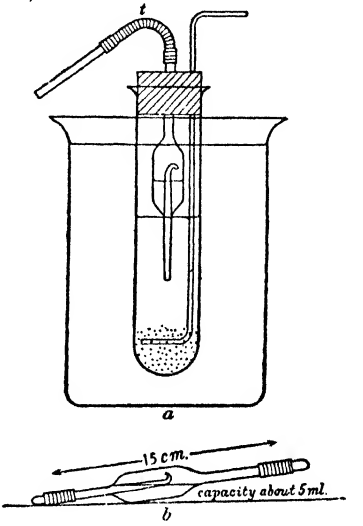


FIG. 37.—Determination of solubility of a solid in a liquid.

Reproduced from Palmer's " Experimental Physical Chemistry " (C.U.P.).

In the case of very sparingly soluble salts the data have been obtained by special methods, *e.g.* electrical conductivity (p. 108).

TABLE OF SOLUBILITIES

Salt.	0°.	15°.	100°.
Potassium iodide	127·5	140	208
„ bromide	53·5	62·5	104
„ chloride	27·6	32·4	56·7
Sodium chloride	35·7	35·9	39·0
Calcium chloride ($CaCl_2$, $6H_2O$)	60	100 (30°)	137 (60°)
Strontium chloride ($SrCl_2$, $6H_2O$)	43	50	—
Barium chloride ($BaCl_2$, $2H_2O$)	31·6	34·4	58·8
Potassium nitrate	13·3	25·8	246
Sodium nitrate	73·0	85	178

TABLE OF SOLUBILITIES—*continued.*

Salt.	0°.	15°.	100°.
Barium hydroxide ($Ba(OH)_2$, $8H_2O$)	1·67	3·23	101·4 (80°)
Calcium hydroxide	0·185	0·170	0·077
Calcium sulphate ($CaSO_4$, $2H_2O$)	0·18	0·279 (40°)	0·260 (60°)
Strontium sulphate	—	0·0011	—
Barium sulphate	—	0·00023	—
Silver chloride	—	0 00015	—
,, bromide	—	0·00001	—
,, iodide	—	0·000000035	—

EUTECTIC POINTS

When a solution freezes usually *pure ice* (or solid *solvent*) separates, all the solute remaining in the liquid. The solution thus becomes increasingly richer in salt (or solute in general), and the freezing point falls, as ice separates. A limit is reached when the solution becomes saturated. On further cooling *ice and solid salt must separate in the same ratio as they exist in solution*; hence the temperature remains constant until all the liquid has solidified.

The minimum temperature reached when solvent and solute separate together on cooling a solution is called the *eutectic temperature* (or *eutectic point*), and the mixture separating is called a *eutectic mixture* (or *eutectic*; Greek *eutēktos*, easily melted). It is shown by microscopic examination and in other ways that the eutectic is a mechanical mixture, although it was thought (by Guthrie in 1875) to be a definite compound or "cryohydrate" (Greek *kryos*, frost).

For a system composed of solution and ice *in the absence of the vapour phase*, the phase rule gives $F = C + 2 - P = 2 + 2 - 2 = 2$, so that the freezing point of a solution depends on pressure and concentration. At the eutectic point, $P = 3$, $\therefore F = 1$, and at a given pressure the freezing point and the concentration of the solution are constant. *In presence of the vapour phase* at the eutectic point $P = 4$, $\therefore F = 0$, and the temperature, vapour pressure and concentration are all fixed. This is called a **quadruple point.**

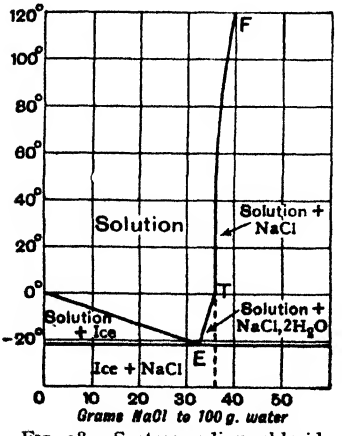


FIG. 38.—System sodium chloride and water.

The curves for sodium chloride and water in Fig. 38 show that pure ice is deposited from dilute solutions until the eutectic point E, $-21·2°$ is reached. This is the lowest temperature of a freezing mixture of solid ice and salt. When a hot saturated solution is cooled, NaCl separates along FT until the temperature falls to 0·15°, when the curve changes direction at a **transition point** T. The hydrate NaCl, $2H_2O$ is deposited along TE until the

eutectic point E is reached, solid NaCl dissolving and (if present in small quantity) finally disappearing in the process. If a large amount of solid NaCl is present, the solution solidifies completely at T.

Freezing-Point Curves of Two Component Systems

The freezing-point curve of a salt solution is a rather specialised case, since it gives results only from the side of pure water, the salt having a high melting point and the miscibility being limited. A more interesting case arises when two components mix in all proportions in the fused state and have melting points not too widely separated. The freezing-point curves then vary considerably for different systems, and were divided by Roozeboom (1899) into *seven main types*. Some systems include two or more of these in one diagram. The seven types are those in which (i) *no compounds or solid solutions are formed*, (ii) *one or more compounds are formed*, (iii)–(vii) five types of diagram when *solid solutions are formed*.

Particularly interesting examples of the freezing-point curves are shown by *binary alloys*, *i.e.* mixtures of two metals. These are of various types: (i) mechanical mixtures of the separate metals, (ii) definite compounds and mixtures of these with excess of a pure metal, (iii) solid solutions, and (iv) combinations of some or all of types (i)–(iii). Other systems besides alloys give similar curves.

Type I. *The two components form no compounds or solid solutions.* Fig. 39 gives the freezing-point curves for antimony and lead. The freezing point of

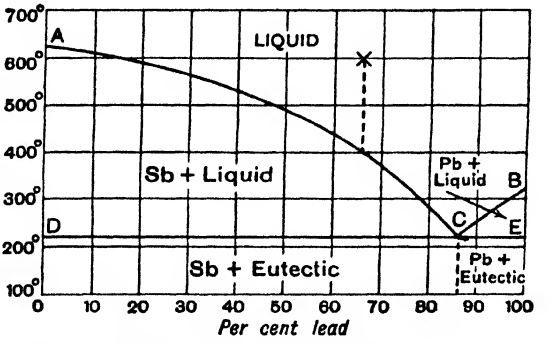


FIG. 39.—Freezing-point curves for antimony and lead.

pure antimony at A is 630·5°, that of pure lead at B is 327·4°. Addition of lead to fused antimony lowers the freezing point progressively along AC till the eutectic point C is reached. In the region ACD solid antimony is in equilibrium with liquid alloys. Addition of antimony to fused lead lowers the freezing point along BC till the eutectic point C is reached. In the region BCE solid lead is in equilibrium with liquid alloys. At C solid lead and solid antimony are in equilibrium with one liquid alloy of the composition of the eutectic mixture. Below DE all is solid.

The points D and E are very close to the temperature axes, but probably not actually on them, when they should correspond with the melting points of pure antimony (A) and lead (B) respectively. In the solid solution diagram (Fig. 42) D and E are markedly separated from the axes; the case now being considered is a special case of this when the miscibilities in the *solid* phases are practically zero.

When liquid alloy represented by X is cooled, solid antimony separates when the temperature reaches the point on AC vertically below X. This separation enriches the liquid in lead, and the freezing point falls progressively along AC till the eutectic C is reached, when lead and antimony separate together till all is solid.

Type II. *One or more compounds are formed.* An example is the system composed of tin and magnesium, which form Mg_2Sn. The freezing-point curve is shown in Fig. 40, in which *atomic* percentages are used.

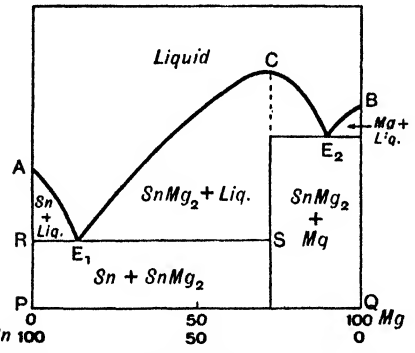


FIG. 40.—Freezing-point curves for tin and magnesium.

The compound Mg_2Sn has a melting point 783·4° represented by C. If pure tin is added to the fused compound the freezing point is lowered. The solid separating along CE_1 is pure Mg_2Sn. Finally a eutectic point E_1 is reached, at which solid Mg_2Sn and tin separate together. If magnesium is added to pure tin, the freezing point falls along AE_1, the solid separating being pure tin until E_1 is reached, when tin and Mg_2Sn separate. The solid obtained on cooling a liquid of composition C will be homogeneous Mg_2Sn. A solid alloy formed from a liquid of composition enclosed within the verticals between C and E_1 consists of crystals of Mg_2Sn embedded in a eutectic mixture of Mg_2Sn and Sn.

On addition of excess of magnesium to Mg_2Sn (or tin to excess of magnesium) a second eutectic point E_2 appears. Between E_2 and B pure magnesium separates, between E_2 and C Mg_2Sn, at E_2 the eutectic Mg_2Sn and magnesium.

On adding to pure tin increasing amounts of magnesium, the freezing-point curve is AE_1CE_2B, with a maximum and two eutectics. A curve of this type is found when one compound is formed. If there are two compounds there will be two maxima, and so on (see the ferric chloride-water system, Fig. 340.) The rounded maximum shows that the compound is partly dissociated in the liquid state.

Solid solutions.—The five solid solution cases may be divided into two groups.

A. The two components form *an unbroken series of solid solutions.* There are three types of curves (which are exactly the same in form as the boiling-point curves in Fig. 34): (I) *the freezing points of all mixtures lie between the freezing points of the pure components*; (II) *the freezing-point curve has a*

maximum; (III) *the freezing-point curve has a minimum.* The solid and liquid in equilibrium differ in composition except at the maximum or minimum, and hence *two* curves are required for each case: (i) the *liquidus curve* (upper full curve), which is the freezing-point curve of the liquid phase, and (ii) the *solidus curve* (lower dotted curve), which is the melting-point curve of the solid phase.

Type I. From the description of the boiling-point curves it should be clear that on cooling a fused mixture Z' of Type I (Fig. 34) of two components A and B, *e.g.* gold and silver, to a', solid b' separates, richer in B than Z', but as the temperature is lowered to Z'' solid b and liquid a are formed. By remelting b' and cooling, a solid (say b'') richer in B than b' is formed; by repeating the process nearly pure B is obtained and the liquid phase tends to become nearly pure A. Thus both pure A and B can be obtained, whereas when solid solutions are not formed, or if there is a eutectic (types I and V) only one pure component can be crystallised out on one side of the eutectic point; when the melt has cooled to this point both components separate together.

On heating the solid Z, liquefaction occurs at c, giving a liquid a''' richer in A than Z. The temperature rises and the compositions of the phases change along a''' a' and cb'. At b' all is liquid.

Type II (not known for alloys). Here fractional crystallisation gives ultimately a solid corresponding with the maximum melting point and the liquid tends to either pure A or B, whichever was in excess above the mixture of maximum melting point. In this case the melting point of one pure component is *raised* by adding the other component.

Type III. Here the solid separating will ultimately be either pure A or B and the liquid tends to the composition for the minimum melting point. This type is known for several alloys.

B. *An unbroken series of solid solutions is not formed.* There are two cases.

Type IV (Fig. 41). In this there is a *transition point.* According as the liquid mixture contains less or more A than the composition corresponding with transition point T (40 p.c. in the figure) it deposits on cooling the solid solutions α or β. At T the liquid is in equilibrium with both α and β of compositions D and E. On cooling, solid β + liquid form solid α. The compositions of solid α and β change on cooling along DF and EG.

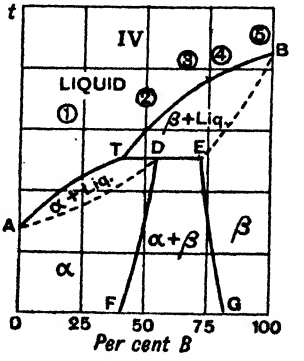


FIG. 41.—Solid solutions with transition point.

Consider the effects of cooling liquid mixtures represented by the points (1) to (5) shown in Fig. 41. From (1) the curve AT is reached and solid solution α separates and finally the whole solidifies to this. On cooling (2) the curve TB is reached and solid solution β separates. When T is reached, solid β at E reacts with liquid at T to give liquid and solid α at D. When AD is reached all is solid α. On further cooling DF is cut, when solid α breaks

down into solid $\alpha+\beta$. On cooling from (3) solid β deposits when TB is cut; when TE is reached liquid at T reacts with solid β at E to give solid α at D and solid β at E; on further cooling solid α and β remain, the compositions varying along DF and EG. Cooling from (4) gives solid β until EG is cut, when β breaks down into $\alpha+\beta$. From (5) only solid β is formed.

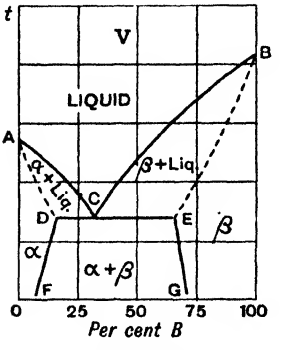


FIG. 42.—Solid solutions with eutectic point.

Type V (Fig. 42). This has a *eutectic point* C and the curves are similar to those in Fig. 39, except that solid solutions α and β are now deposited of compositions corresponding with D and E. C is a eutectic point, where solid α and β deposit together. On further cooling the solid, these change composition along DF and EG.

Cooling curves.—Phase diagrams are easily constructed by **Tammann's method.** Various mixtures of the metals are melted in a silica crucible and the liquid allowed to cool slowly. The temperatures are measured by a thermocouple and temperatures plotted against times.

Consider the case of two metals which form no compounds or solid solutions. When the two pure metals cool the temperature falls regularly to the freezing point when (apart from initial supercooling) it remains constant (owing to the evolution of latent heat) till all is solid, when it falls again. Curves A and B (Fig. 43, lower diagram) are obtained. With the eutectic mixture a similar result is obtained and curve C is found, the solid now being a mixture of the two metals. With other mixtures, *one* of the metals first separates and the curve shows a break since heat is again evolved. The horizontal corresponding with the eutectic is also shorter, and if the lengths of the horizontals at the eutectic temperature are assumed proportional to the amount of eutectic mixture, and plotted as in the upper diagram, the position of the eutectic is found and hence the approximate freezing-point curves ACB. The method can be used with other types of freezing-point curves.

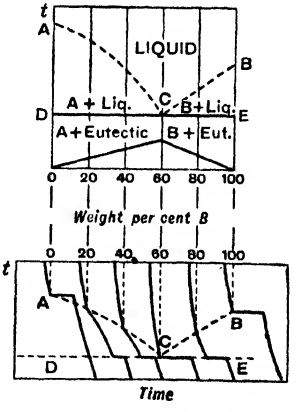


FIG. 43.—Cooling curves.

FREEZING POINTS OF SOLUTIONS

The freezing point of a salt solution is lower than that of pure water; sea water freezes at about $-2°$. Bishop R. Watson in 1771 found that the times taken for solutions of various salts to begin to freeze when exposed to cold air, reckoned from the time when water began to freeze, were proportional to the

quantities of dissolved salt; hence: "in salt of the same kind, the resistance to congelation is in direct simple proportion to the quantity of salt dissolved". The result that *the lowering of freezing point is proportional to the amount of dissolved substance in a given quantity of solvent* was again found by Blagden in 1788, and is often called *Blagden's law.*

If m is the amount of dissolved substance in a given weight of solvent, and D the freezing-point lowering:

$$D/m = const.$$

This relation, which is true only for dilute solutions, is shown by the figures below for cane sugar in water; m is in g. mols. (mols) per 1000 g. of water.

m	D	D/m
0·000344	0·000645	1·875
0·000995	0·001867	1·876
0·002303	0·004332	1·881
0·004278	0·007957	1·861
0·01026	0·01906	1·858
0·01841	0·03434	1·866
0·0365	0·06793	1·862

Raoult * in 1883 found experimentally that *quantities of different substances in the ratio of the molecular weights, when dissolved in identical weights of the same solvent, give solutions of identical freezing point.*

A mol (mol. wt. in g.) of a substance dissolved in 1 kg. (1000 g.) of a given solvent thus depresses the freezing point by a constant amount, which is called the **molecular depression of freezing point**, Δ.

Solvent	Δ	M.p.	Solvent	Δ	M.p.
Water -	1·858°	0°	Formic acid	2·8°	8°
Acetic acid -	3·9°	17°	Phenol -	7·27°	40°
Benzene -	4·9°	5°	Camphor -	40°	180°

Van't Hoff in 1886 showed that Δ is related to the latent heat of fusion per g., l_f, and the absolute melting point T_f, of the solvent by the formula:

$$\Delta = \mathbf{R}T_f^2/1000l_f. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(3)$$

For water: $l_f = 79{\cdot}77$, $T_f = 273{\cdot}1$; also $\mathbf{R} = 1{\cdot}988$ g. cal./1° C.

$$\therefore\ \Delta = 1{\cdot}988 \times (273{\cdot}1)^2/(79{\cdot}77 \times 1000) = 1{\cdot}858°.$$

Let the depression of freezing point produced by w g. of solute in W g. $= W/1000$ kg. of solvent be D; this is produced by $1000\ w/W$ g. of solute in 1 kg. of solvent. The depression produced by the g. mol. wt. M in 1 kg. of solvent is Δ, the molecular depression, and the depressions are in the ratio of the amounts of solute in 1 kg. of solvent, hence:

$$(1000\ w/W)/M = D/\Delta;$$

$$\therefore\ M = 1000\ w\Delta/WD. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(4)$$

* See the volumes *Détermination des poids moléculaires* and *La dissolution* in the series *Les Classiques de la découverte scientifique* (Paris, Gauthier-Villars).

EXAMPLE.—1·35 g. of carbon tetrachloride dissolved in 55 g. = 55/1000 kg. of glacial acetic acid depressed the f.p. from 16·750° to 16·132°; ∴ $D = 0·618°$. Δ for acetic acid is 3·9°;

$$\therefore M = 1·35 \times 3·9 \times 1000/55 \times 0·618 = 155 \quad (CCl_4 = 153).$$

Raoult's law of depression of freezing point holds only:

(i) for *dilute* solutions, hence Δ should be *calculated* by (4) from results found with dilute solutions:

$$\Delta = MWD/1000\,w;$$

(ii) when *pure solid solvent separates* on freezing, not solid solutions;

(iii) for *non-electrolytes*, since ionised electrolytes give abnormally low values of M (see p. 80).

Determination of molecular weights by the freezing-point method.—Although quite serviceable results can be obtained in elementary work with a test-tube containing the solution, a stirrer, and a thermometer graduated in 0·1°, more accurate experiments require special apparatus and a *Beckmann thermometer*. This (Fig. 44) has a large bulb *B* and only six degrees on the scale *S*, which is graduated in $\frac{1}{100}$ degrees. There is a reservoir *b* at the top into which mercury can be shaken if higher temperatures are used, or from which mercury can be drawn (by warming the bulb until the mercury thread enters the reservoir) if lower temperatures are used. The actual readings on the scale do not matter, as only their *difference* is wanted.

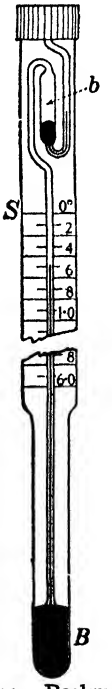


FIG. 44.—Beckmann thermometer.

Reproduced from Palmer's "Experimental Physical Chemistry" (C.U.P.).

About 20 g. of solvent are weighed into the tube *A* (Fig. 45) and a bent wire stirrer and the thermometer are fitted through a cork, so that the thermometer bulb is covered with the liquid.

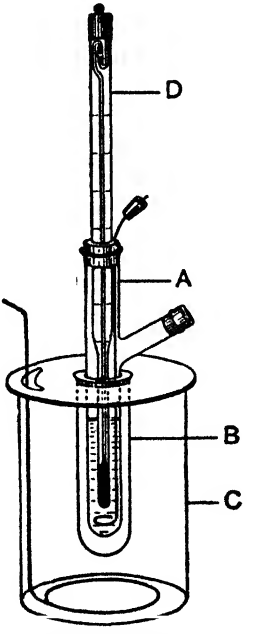


FIG. 45.—Beckmann freezing-point apparatus.

The tube *A* is fitted through a cork into a large test-tube *B*, which serves as an air-jacket and prevents too rapid fall in temperature. It is supported in a freezing mixture in the large jar *C*.

The stirrers in the solvent tube and outer jar are worked and the thermometer observed. The mercury falls to a point when the solvent is slightly supercooled. Freezing then begins and the temperature runs up to the freezing point, when it remains steady. It is read with a lens, the thermometer being gently tapped to prevent adhesion of mercury to the glass. Suppose the reading is 3·216° (the last figure being estimated).

The tube *A* is taken out and allowed to warm until the solvent liquefies. A weighed quantity of the substance is put in through the side tube and dissolved by working the stirrer. The tube is replaced in the air-jacket and put into the freezing mixture. The freezing point of the solution is determined in the same way as that of the solvent. Suppose this to be 2·839°, then *D*, the depression of freezing point, is $3{\cdot}216 - 2\ 839 = 0{\cdot}377°$.

A freezing mixture of ice and salt is used if the solvent is water; ice and water are used for benzene, acetic acid, and formic acid; phenol is melted in warm water and the inner tube and air-jacket supported in a clamp without outer jar. Acetic and formic acids and phenol readily absorb moisture, which lowers their freezing points, and care must be taken to prevent this during the experiment.

In accurate work a correction is applied for supercooling, since when the solution freezes some ice separates and the concentration of the remaining solution is higher than before freezing.

The freezing-point method is sometimes called the *cyroscopic method* (Greek *kryos*, frost, and *skopeo*, I observe). It is much more accurate than the other methods for the determination of molecular weights in solution (vapour pressure, boiling point, and osmotic pressure), although in very exact work special apparatus is required. Pure water and the solution are contained in separate vessels, each with an immersed platinum resistance thermometer, and the vessels surrounded by air-jackets. The water is immersed in a bath of pure ice and water, and the solution in a bath of ice and brine slightly below the freezing point. The two sides are frozen by evaporating ether in the air spaces, and kept stirred, the heating effect of this being the same on both sides.

Vapour Pressures of Solutions

When a non-volatile substance is dissolved in a volatile solvent, *e.g.* salt in water, the vapour pressure of the solution is lower than that of the pure solvent (p. 50). If p_0 is the vapour pressure of the pure solvent and p that of the solution, at the same temperature, the fraction $(p_0 - p)/p_0$ is called the *relative lowering of vapour pressure*. It was found by von Babo (1848) and Wüllner (1856) to be approximately proportional to the amount of substance dissolved in a fixed weight of solvent, and practically independent of temperature within certain limits.

Raoult in 1887 then showed by experiment that the relative lowering of vapour pressure for a solution containing N mols of solvent and n mols of solute is:

$$(p_0 - p)/p_0 = n/(N + n), \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

where N is calculated as the weight of solvent W g. divided by its molecular weight M *in the state of vapour*: $N = W/M$. If w g. of solute are present and its molecular weight is m, then $n = w/m$, hence from (5) the value of n and thus of m can be found.

Equation (5) can also be written as:

$$p = p_0 \cdot N/(N+n) = p_0 N_1, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5a)$$

where $N_1 = N/(N+n)$ is the *mol fraction* of the solvent in the solution, *i.e.* the number of mols of solvent divided by the total number of mols of solvent and solute.

EXAMPLE.—Pure benzene C_6H_6 ($M = 78$) has the vapour pressure $p_0 = 751{\cdot}86$ mm. at 80°. A solution of 2·47 g. of ethyl benzoate in 100 g. $= 100/78 = 1{\cdot}282$ mols $= N$ of benzene has the vapour pressure $p = 742{\cdot}60$ mm. at 80°. Thus

$$(p_0 - p)/p_0 = (751{\cdot}86 - 742{\cdot}60)/751{\cdot}86 = 0{\cdot}0123;$$
$$\therefore\ 0{\cdot}0123 = n/(1{\cdot}282 + n); \quad \therefore\ n = 0{\cdot}01597.$$

Let m = mol. wt. of ethyl benzoate, then $n = 2{\cdot}47/m$;

$$\therefore\ m = 2{\cdot}47/0{\cdot}01597 = 154{\cdot}6 \quad (C_6H_5COOC_2H_5 = 150).$$

The relation between lowering of vapour pressure and depression of freezing point is shown in Fig. 46. OA is the vapour pressure curve of the pure solvent.

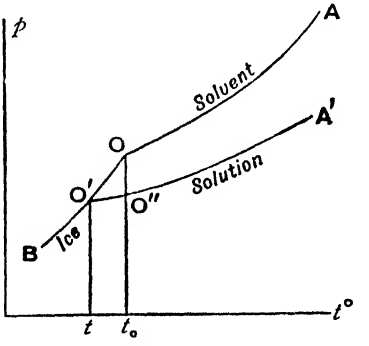


FIG. 46.—Vapour pressure curves of solvent, solution, and ice.

At the freezing point t_0 this cuts the vapour pressure (sublimation) curve of ice OB, which has a different slope (exaggerated in the figure), at O. The vapour pressure curve of the solution O'A' lies below that of the solvent and cuts the ice curve at O', which is the freezing point t of the solution where solution and ice are in equilibrium, each having the same vapour pressure. If this were not the case distillation would occur between ice and solution and there could not be equilibrium.

For small depressions OO' and O'O'' are practically straight lines and hence OO'' is proportional to O'O'', *i.e.* to $t_0 - t$. Hence *the depression of freezing point is proportional to the lowering of vapour pressure.*

The direct measurement of vapour pressure is difficult and the method is not much used. Raoult's apparatus consisted of two barometer tubes A and B

(Fig. 47), and a third tube C, fitted by rubber stoppers into an iron receiver D, which was connected with a mercury reservoir by pressure tubing at *E*. The tubes were placed in a tank of water with a glass window. The air-free solvent and solution were introduced through capillaries at the tops of the tubes B and A, which were afterwards sealed off. The tube C was connected with an air reservoir at a known pressure lower than atmospheric. The difference of levels in A and B was read by a cathetometer, and since the pressure in C was known, the absolute vapour pressures were found. The difference gives $p_0 - p$.

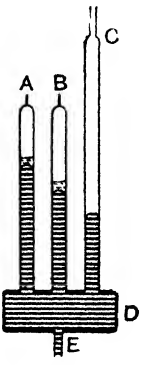


FIG. 47.—Raoult's vapour pressure apparatus.

In a more convenient method used by Walker (1888) a slow stream of dry air is bubbled through the solution in three Liebig's potash bulbs, and then through pure water (or other solvent) in three further bulbs. The air is first saturated to the partial pressure p by the solution, and then to the partial pressure p_0 by the solvent. The losses in weight of the solution and solvent bulbs are in the ratio $p/(p_0 - p)$, and by weighing the bulbs before and after the experiment $(p_0 - p)/p_0$ is found. In Partington's method (*J.C.S.*, 1911, **99**, 466) the moisture is absorbed from the air in weighed drying tubes behind the solution and solvent bulbs separately, and this gives more accurate results.

Deliquescence.—The lowering of vapour pressure in *concentrated* solutions (which do not obey Raoult's law) may be large and the vapour pressure may fall below the partial pressure of moisture in the air, which is usually about 66 p.c. of the saturation pressure at a given temperature. A saturated solution has the lowest vapour pressure possible, and if the salt is very soluble this may be small. The salt attracts moisture from the air and partly liquefies to some saturated solution. This attracts more moisture and more saturated solution is formed until finally the whole is liquid. This liquefaction of very soluble salts on exposure to moist air is called **deliquescence**. It is shown *e.g.* by caustic alkalis, potassium carbonate, calcium chloride, and ferric chloride. Solids which attract moisture without liquefaction, and liquids like sulphuric acid which absorb moisture, are called *hygroscopic substances*. Solutions of calcium chloride are used in " air conditioning " to produce a regulated humidity.

BOILING POINTS OF SOLUTIONS

Since the boiling point is the temperature at which the vapour pressure reaches atmospheric pressure, a lowering of vapour pressure will mean a higher boiling point. Aqueous salt solutions boil above 100°.

A solution, *e.g.* of calcium chloride boiled in an iron pan, may be used as a heating bath in the laboratory:

g. $CaCl_2$ in 100 g. water	50	200	325
b.p. - - - - -	112°	158°	180°

The boiling points of solutions were studied in 1871 by Raoult, who found that: (i) *the elevation of boiling point is proportional to the amount of solute dissolved in a given weight of solvent*, and (ii) *equimolecular amounts of different substances dissolved in identical weights of the same solvent produce equal elevations of boiling point.*

The **molecular elevation of boiling point** E is *the rise in b.p. for* 1 *mol of non-volatile solute in* 1 *kg.* (1000 g.) *of solvent.*

If w g. of solute of molecular weight M are dissolved in W g. $= W/1000$ kg. of solvent, and D is the elevation of b.p., Raoult's first result shows that:

$$D/E = \frac{1000\,w}{W} \Big/ M;$$

$$\therefore\ M = 1000\,wE/WD. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (6)$$

The values of E for some solvents are given below.

	B.p.°C.	E
Water - - -	100	0·52
Methyl alcohol - -	64·7	0·88
Ethyl alcohol - -	78·3	1·15
Ether - - -	35·4	2·10
Benzene - - -	80·2	2·57
Chloroform - -	61·2	3·66

E may be calculated from the latent heat of evaporation of the solvent per g., l_e, in a similar way to Δ from the latent heat of fusion (p. 69). If T is the absolute boiling point

$$E = \frac{RT^2}{1000\,l_e} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (7)$$

For water, $T = 100 + 273 = 373$, $l_e = 539$.

$$\therefore\ E = 1{\cdot}988 \times (373)^2 \div (539 \times 1000) = 0{\cdot}513 \text{ (obs. } 0{\cdot}516).$$

The equations do not hold for concentrated solutions, and the molecular weights of electrolytes are abnormal in solution.

EXAMPLE.—2·0579 g. of iodine dissolved in 30·14 g. of ether gave an elevation of boiling point of 0·566°.

$w = 2{\cdot}0579$, $W = 30{\cdot}14$, $D = 0{\cdot}566°$, $E = 2{\cdot}10°$;

$\therefore\ M = (1000 \times 2{\cdot}0579 \times 2{\cdot}10)/(30{\cdot}14 \times 0{\cdot}566) = 253{\cdot}3$. But $I_2 = 2 \times 126{\cdot}9 = 253{\cdot}8$,

$\therefore$ iodine exists as diatomic molecules I_2 in solution in ether.

Determination of elevation of boiling point.—The apparatus used by Beckmann to determine the boiling points of solutions is described in books on physical chemistry. It is difficult to use and has been replaced by a large number of other methods, one of which will be described here.

McCoy's apparatus consists of an outer tube A containing some of the solvent and a graduated inner tube B which is fitted with a Beckmann thermometer (Fig. 48). About 15 c.c. of solvent are put into B and the solvent in A is boiled, the clip c being closed. The vapour passes into B through the inner tube ab,

open to the vapour in *A* at *a* and ending in a perforated bulb at *b*. The vapour condenses and raises the solvent in *B* to the boiling point, a slow distillation taking place through the condenser *C*. The boiling point of the solvent is read off.

The clip *c* is now opened (to prevent liquid being drawn back from *B* into *A*) and the boiling stopped. A weighed amount of substance is added to *B* by taking out the cork and thermometer, which are then replaced. The clip *c* is closed and the liquid in *A* again boiled. The vapour condenses in the solution in *B* and the latent heat evolved raises it to the boiling point.

When the temperature is steady *c* is opened, the thermometer taken out, and the volume of the solution in *B* read. Since *B* is enclosed in a vapour jacket the amount of condensation necessary to raise the solution to its boiling point is small.

The molecular weight is calculated by the formula :

$$M = K\frac{w}{Dv} \quad \ldots\ldots\ldots\ldots\ldots\ldots (8)$$

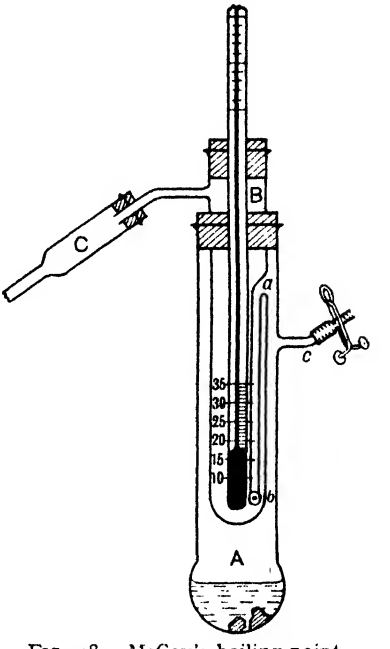


FIG. 48.—McCoy's boiling point apparatus.

where w = wt. of solute in g., v = vol. of solution in c.c., D = observed elevation of boiling point, K = a constant = $1000E/d$, where d = density. The values of K for some solvents are : water 540, alcohol 1560, acetone 2200, benzene 3280, ether 3030.

OSMOTIC PRESSURE

The *diffusion* of substances in solution (p. 27) shows an analogy with the diffusion of a gas, the dissolved molecules tending to spread through the liquid solvent.

A drop of copper sulphate solution introduced by a pipette into a solution of potassium ferrocyanide is covered with a thin pellicle of copper ferrocyanide $Cu_2Fe(CN)_6$ which is *semipermeable*, *i.e.* allows only water but not dissolved salts to pass through it. The drop expands or contracts as water passes through the pellicle, the direction of passage depending on the concentrations of the solutions (M. Traube, 1867).

EXPT. 5.—An interesting experiment is the *chemical garden*, described by Glauber in 1648. In a solution of sodium silicate of s. g. 1·1, made by diluting water glass, small pieces of ferric, nickel, cobalt and cupric chlorides are placed. After a few hours long filaments of gelatinous silica coloured by the metal

hydroxides grow from the crystals. A semipermeable film forms round each crystal, water enters and bursts the film, and the solution driven out forms a new film, and so on (Fordham and Tyson, *J.C.S.*, 1937, 483).

The copper ferrocyanide membrane is too weak to support a pressure, so Pfeffer in 1877 deposited it in the wall of an unglazed earthenware porous pot.

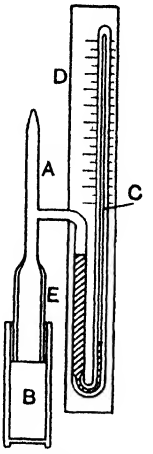


FIG. 49.—Measurement of osmotic pressure.

The semipermeable membrane can be formed in the walls of the pot as follows (Adie, *J.C.S.*, 1891, **59**, 344). The clean and dry pot *B* (Fig. 49) with the glass tube *E* fixed in with sealing wax is gradually lowered into copper sulphate solution whilst the potassium ferrocyanide solution is being poured into the inside. The pot is then placed in a vacuum for some days to draw the air from the pores, and allowed to stand about three weeks in more dilute solutions. It is then attached to the manometer *C* by sealing on the tube *A*, is filled with solution, and placed in water. When the pressure developed reaches a maximum it is read off. This is called the *osmotic pressure* of the solution.

Morse (1901) prepared the membranes by filling the pot (the pores of which were filled with water) with potassium ferrocyanide solution and immersing it in copper sulphate solution, and then electrolysing it with a copper anode outside the pot and a platinum cathode inside. The $Cu^{"}$ and $Fe(CN)_6^{""}$ ions moved towards one another in the wall of the pot and formed a film of copper ferrocyanide. As the copper ions move faster, the film is formed near the inner surface of the pot. Morse showed that the membrane was impervious to sugar for 60 days at an osmotic pressure of 12 atm., but allowed water to pass.

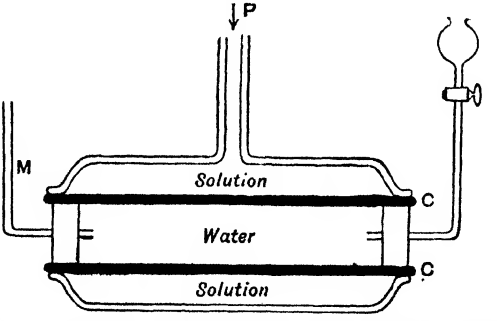


FIG. 50.—Apparatus of Berkeley and Hartley (diagrammatic).

Lord Berkeley and Hartley (*Proc. Roy. Soc.*, 1904, **73**, 436; *Phil. Trans.*, 1906, **206**, 481; Vegard, *Phil. Mag.*, 1908, **16**, 247, 396) measured the osmotic pressures of concentrated solutions with an apparatus (Fig. 50) in which the porous tube *C* carrying the semipermeable membrane is filled with water and surrounded by the solution to which a pressure *P* is applied to balance the

osmotic pressure. The two pressures are equal when no water passes through the membrane, the meniscus in *M* remaining stationary. The membrane is subjected to equal pressures on both sides and hence is less likely to fail under the high pressures measured. In this method the pressure is applied mechanically to the solution, whilst in Pfeffer's method it is set up by solvent entering the closed pot.

The osmotic pressure of a solution may be defined as the pressure which must be applied to the solution to prevent solvent passing into it through a perfect semipermeable membrane, *i.e.* one which is mechanically rigid and permeable only to the pure solvent. Osmotic pressures are quite large (several atm.) for moderately concentrated solutions, and pressures of 131 atm. have been measured for concentrated solutions. The *laws of osmotic pressure* were discovered (from Pfeffer's results) by van't Hoff in 1885.

Pfeffer had already shown that *the osmotic pressure at a given temperature is proportional to the concentration.* This corresponds with *Boyle's law* for gases (since $V = 1/C$).

Osmotic pressures of cane-sugar solutions at 0°

Concentration C g./lit. soln. -	10·03	20·14	40·60	61·38
Osmotic pressure P atm. - -	0·686	1·34	2·75	4·04
Ratio P/C - - - - -	0·068	0·067	0·068	0·066

With more concentrated solutions the ratio P/C increases with concentration. Morse (1912) found for sugar solutions at 20° that it increased from 0·077 for $C = 34{\cdot}2$ g. per 1000 g. water to 0·0944 for 342·2 g. per 1000 g. water, although he found that the proportionality is much closer when C is so expressed than when it is expressed in g. per lit. of solution.

The effect of temperature on osmotic pressure was also investigated by Pfeffer.

Osmotic pressures of 1 *per cent. cane-sugar solution*

P atm. - - - -	0·648	0·691	0·721	0·746
Abs. temp. T - - -	273	286·7	295·0	309·0
$(P/T) \times 10^3$ - - -	2·37	2·41	2·44	2·41

The results show that *the osmotic pressure at a given concentration is proportional to the absolute temperature.* This corresponds with *Charles's law* for gases.

The following calculation was made by van't Hoff (see *Alembic Club Reprint* No. 19) :

The mean value of P/C at 0° C. is 0·066 ; this is the osmotic pressure in atm. exerted by 1 *gram* of sugar in 1 litre of solution. Since the molecular weight of sugar is 342, this is also the pressure exerted by 1 *gram molecule* of sugar in 342 litres. The pressure is proportional to the concentration, hence it becomes 1 atm. when the volume containing 1 gram molecule (mol) is $342 \times 0{\cdot}066 = 22{\cdot}6$ litres. 1 mol of ideal gas in 22·4 litres at 0° exerts a pressure of 1 atm. The value 22·6 for a molar solution is nearly 22·4, and hence *the*

osmotic pressure is equal to the pressure which the solute would exert if it were an ideal gas occupying the same volume as the solution. The result also shows that dilute solutions obey *Avogadro's law*, since the figures show that

$$PV/T = 0{\cdot}066 \times 342/273 = 0{\cdot}0827 \text{ lit. atm. per } 1°,$$

which is close to the value of the gas constant $\mathbf{R} = 0{\cdot}0821$ lit. atm. per 1° (p. 13).

The osmotic pressure of a *dilute* solution thus obeys the gas law :

$$PV = \mathbf{R}T, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(9)$$

As actual gases deviate increasingly from this at higher pressures, so do actual solutions. It is found that for concentrated solutions the equation

$$P(V - b) = \text{const.},$$

where b is a constant analogous to that in van der Waals' equation (p. 35), gives good results.

Isotonic solutions.—An ingenious method of *comparing* osmotic pressures was devised by de Vries in 1884. He noticed on examining a slice of living plant tissue in a concentrated salt solution under the microscope that the protoplasm content of cells contracted. This effect is called *plasmolysis*. The protoplasm is surrounded by a thin wall which acts as a semipermeable membrane, and when the osmotic pressure of the solution outside is greater than that of the natural solution inside, water is forced out of the protoplasm, which shrinks from the rigid cell wall. If the osmotic pressure outside is less than that inside, the protoplasm takes up water and swells, whilst if the pressures are equal there is no effect.

By making up solutions of equal osmotic pressure, called *isotonic solutions*, having the same osmotic pressure as the cell content, they were found to contain quantities of dissolved substances in the ratio of the molecular weights for non-electrolytes, but isotonic solutions of electrolytes contained equal numbers of particles (ions + molecules) in equal volumes.

Relation between osmotic pressure and vapour pressure lowering.—The laws of osmotic pressure, vapour pressure and freezing point lowerings, and elevation of boiling point are all connected, so that if one is given the others may be found. This was shown for osmotic pressure and vapour pressure lowering by Gouy and Chaperon (1888) and by Arrhenius (1889) as follows.

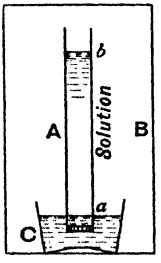


FIG. 51.—Osmotic pressure and vapour pressure.

Let a solution in a tube A (Fig. 51) closed below by a semipermeable membrane be put in contact with pure solvent in C, enclosed in a vessel B containing only solvent vapour. A column of solution *ab* of height h is supported by the osmotic pressure.

The *vapour pressure* at a is that of the solvent $= p_0$, and is greater than that of the solution p at b by the weight of the column of solvent vapour of height h :

$$\therefore\ p_0 - p = hd = hpM/\mathbf{R}T, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(10)$$

where d = density of vapour $= pM/\mathbf{R}T$ where M = mol. wt. of vapour ($d = M/V$).

The *osmotic pressure* is :

$$P = hD = \mathbf{R}T/V, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (11)$$

where D = density of the dilute solution, approximately that of the pure solvent and V = vol. of solution containing 1 mol of solute. If the solution contains N mols of solvent and n mols of solute, $V = NM/Dn$; $\therefore$ from (11) :

$$hD = \mathbf{R}TDn/NM. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (12)$$

Substitute h from (12) in (10) ;

$$\therefore\ p_0 - p = np/N,$$

which by rearrangement gives Raoult's equation (5), p. 71 :

$$(p_0 - p)/p_0 = n/(N + n).$$

Relation between osmotic pressure and freezing point lowering.—From Fig. 46 it was shown that the depression of freezing point is proportional to the lowering of vapour pressure. But equations (10) and (11) show that this is proportional to the osmotic pressure, hence *the freezing point lowering is proportional to the osmotic pressure.* The freezing point equation was deduced from the osmotic pressure equation by van't Hoff (1886).

Take a large mass A of solution containing n mols of solute in W g. of solvent, at its freezing point $T - \Delta T$, where T is the absolute freezing point of the pure solvent and ΔT the freezing point lowering. The solution is contained in a cylinder with a piston (Fig. 52) and can be put in contact through a semi-permeable base a with pure solvent B. The piston is balanced by the osmotic pressure P. Carry out the following reversible cycle :

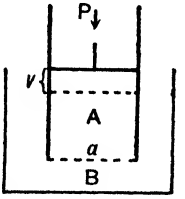


FIG. 52.—Osmotic pressure and freezing point.

(1) Freeze out a quantity of solvent containing 1 mol of solute in the solution, *i.e.* W/n g.

(2) Warm the ice to T and allow it to melt. Heat $l_f W/n$ is absorbed, where l_f = latent heat of fusion of ice.

(3) Warm the solution to T, put the cylinder in contact with the solvent through a and allow W/n g. of solvent of volume V to enter. The work done is $PV = \mathbf{R}T$.

(4) Cool the solution to $T - \Delta T$ and the cycle is complete.

The Second Law of Thermodynamics states that the work done in the cycle ($\mathbf{R}T$) is equal to the heat absorbed at the higher temperature ($l_f W/n$) multiplied by $\Delta T/T$:

$$\therefore\ \mathbf{R}T = l_f \frac{W\Delta T}{nT};$$

$$\therefore\ \Delta T = \frac{\mathbf{R}T^2 n}{l_f W}. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (13)$$

This shows that the depression of freezing point is proportional to n/W or the number of mols of solute in a given mass of solvent. If $n = 1$, $W = 1000$, then $\Delta T = \Delta$, the molecular depression of freezing point, and the equation is identical with (3) on p. 69.

Electrolytes

In solutions of electrolytes (see Chap. IV) the osmotic pressure, depression of freezing point, lowering of vapour pressure, and elevation of boiling point are all abnormally large, so that the molecular weights calculated from them are too small. Arrhenius (1887) explained this as due to *electrolytic dissociation*. The osmotic properties are proportional to the number of solute particles and dissociation increases this number, hence a smaller quantity of electrolyte than 1 mol produces the same effect as 1 mol of a non-ionised or *normal* solute.

If the observed osmotic pressure is P' and the normal value is P, the ratio P'/P is called *van't Hoff's factor* i, and it is also equal to D'/D where D' and D are the observed and normal depressions of freezing point or elevations of boiling point, since these have been shown above to be proportional to the osmotic pressures.

If electrolytes obeyed the same laws as non-electrolytes the *degree of dissociation* α into ions could be calculated from i. Let n ions be formed from one molecule of electrolyte on *complete* ionisation, then one mol of electrolyte gives $(1-\alpha)$ mols of non-ionised electrolyte and $n\alpha$ mols of ions, making $1+(n-1)\alpha$ mols in all.

$$P'/P = D'/D = i = 1 + (n-1)\alpha\,;$$

$$\therefore\ \alpha = \frac{i-1}{n-1}. \qquad \text{.....(14)}$$

Since the osmotic pressure, vapour pressure, boiling point and freezing point methods are all connected by thermodynamics they must all necessarily give the same value of i. On Arrhenius's theory, however, the ratio of the *equivalent electrical conductivities* (p. 108) at a given dilution and at infinite dilution, respectively, should give an independent value of α:

$$\frac{\lambda}{\lambda_\infty} = \alpha. \qquad \text{.....(15)}$$

The following table shows that there is *approximate* agreement only between the two values of α.

Substance	Concentration g. equiv./lit.	α from freezing point (14)	α from conductivity (15)	n
KCl	0·01	0·946	0·943	2
	0·02	0·915	0·924	
	0·05	0·890	0·891	
	0·10	0·862	0·864	
K_2SO_4	0·001	0·939	0·957	3
	0·01	0·887	0·873	
	0·10	0·748	0·716	
$BaCl_2$	0·001	0·949	0·959	3
	0·01	0·903	0·886	
	0·10	0·798	0·754	
$K_3Fe(CN)_6$	0·001	0·946	0·930	4
	0·01	0·865	0·822	
	0·10	0·715	—	

The modern theory of strong electrolytes (Chap. IV) gives a different interpretation of these results. It assumes that *in dilute solutions all strong electrolytes are completely ionised.* The abnormal changes in osmotic pressure and freezing point with concentration are then regarded as due to interionic attractive forces which *reduce* the osmotic pressure, just as the attractions between gas molecules reduce the pressure (p. 35).

Let P_i be the *ideal* osmotic pressure calculated on the assumption that a strong electrolyte giving n ions per molecule is *completely ionised* at a concentration c mols./lit. $= 1/V$; we have $\alpha = 1$, $\therefore\ i = n$;

$$\therefore\ P_i = ncRT \quad \text{.....(16)}$$

If P is the *observed* osmotic pressure, the ratio P/P_i is less than 1 but approaches 1 at infinite dilution, and is called the *osmotic coefficient* g :

$$P/P_i = D/D_i = g \quad \text{.....(17)}$$

(the osmotic pressure ratio is equal to the ratio of the observed and ideal freezing point lowerings D and D_i).

The theory of Debye and Hückel (p. 110) shows that

$$1 - g = 0{\cdot}265\phi\sqrt{nc} \quad \text{.....(18)}$$

for water at 0°, where ϕ is a *valency factor* having the following values for the types of electrolytes shown :

	KCl	$CaCl_2$	$CaSO_4$	$AlCl_3$
Valencies	1, 1	2, 1	2, 2	3, 1
n - -	2	3	2	4
ϕ - -	1	$2\sqrt{2}$	$4\sqrt{4}$	$3\sqrt{3}$

(The values of n are the numbers of ions from 1 molecule of electrolyte.) Thus for (1, 1-valent) electrolytes such as KCl in water at 0° :

$$1 - g = 0{\cdot}375\sqrt{c} \quad \text{.....(19)}$$

From (17) and (18) it follows that :

$$D = D_i(1 - 0{\cdot}265\phi\sqrt{nc}) \quad \text{.....(20)}$$

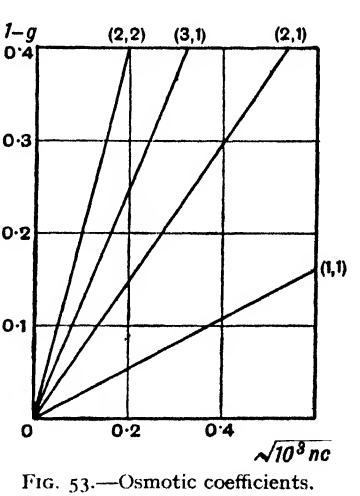


FIG. 53.—Osmotic coefficients.

The values of $1 - g$ are plotted in Fig. 53 against $\sqrt{10^3 nc}$, and it is seen that the curves differ according to the valency type, a behaviour which is quite foreign to the classical theory of Arrhenius. Since the ratio λ/λ_∞ is given by a different equation (p. 112), it cannot be expected to be equal to D'/D.

It should be noted that the simple Debye and Hückel equations apply only to *very dilute* solutions of electrolytes, just as the simple van't Hoff equation (9), p. 78, applies only to very dilute solutions of non-electrolytes. In the case of more concentrated solutions, as in that of gases at higher pressures (p. 35), various corrections must be applied.

Colloids

Liquid diffusion.—Liquid diffusion, which gives evidence of molecular motion in liquids (p. 27), was investigated by Graham (1850–62). He placed small bottles containing solutions in large jars of water (Fig. 54), and determined by analysis the amount of substance diffusing into the water in a given time.

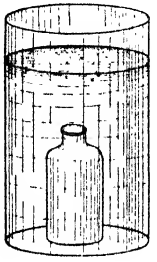


Fig. 54.—Graham's experiment on liquid diffusion.

Acids and salts diffused quickly; glue, starch, and albumin only very slowly. The rapidly diffusing substances were (except acids) all crystalline, and were called **crystalloids** by Graham. Gum and albumin form amorphous solids like glue and were called **colloids** (Greek *kolla*, glue). The differences were so great that Graham differentiated "two worlds of matter, the crystalloid and the colloid," each with characteristic properties.

Substance	Times of equal diffusion	Amounts diffusing in equal times
Sodium chloride	100	100
Ammonia	160	85
Alcohol	200	47
Glucose	300	36
Gum arabic	700	0·8
Albumin	2100	0·3

Expt. 6.—The rates of diffusion of crystalloids and colloids may be shown by pouring solutions of various coloured substances into test-tubes half filled with 1 per cent. agar jelly and noting how far the colour has penetrated in 24 hours. $K_2Cr_2O_7$, $CuSO_4$ and methyl violet diffuse rapidly; gold sol and the dyes Congo red and night blue hardly diffuse at all.

If sodium dichromate solution is diffused into an agar gel containing lead acetate a series of yellow bands of lead chromate called *Liesegang bands* are formed. They are obtained with many other pairs of salts forming precipitates.

Dialysis.—In other experiments Graham placed a solution in a shallow bell-jar closed below by a piece of parchment paper or bladder (a solid colloid), separating the solution from pure water in which the apparatus, called a **dialyser** (Fig. 55), was placed. Crystalloids passed through readily, but colloids did not pass through at all, or only exceedingly slowly.

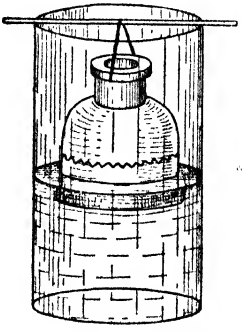


Fig. 55.—Graham's dialyser.

A convenient dialyser is a parchment paper or cellulose ("sausage-skin") tube bent into a U-shape and placed in a jar through which a slow stream

of water passes (Fig. 56). Small thimbles of parchment paper or collodion slipped over the end of a glass tube and fixed by a short length of rubber tubing may be used.

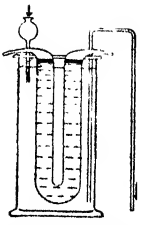


FIG. 56.—Tubular dialyser.

EXPT. 7.—Pour a solution of potassium iodide and starch into a dialyser dipping into distilled water. After half an hour add chlorine water to the water in the dish. A yellow colour of iodine shows that the iodide has diffused through the parchment paper, but the starch is retained since this would have given a blue colour with the iodine, as may be seen by adding chlorine water to the liquid in the dialyser.

Molecular weights of colloids.—The slow rates of diffusion and dialysis suggest that *colloids have high molecular weights*; this was recognised by Graham, and is confirmed by experiment.

(i) If the colloid is acidic or basic its molecular weight is found by *neutralisation* to be high.

(ii) The depressions of *freezing point* give the molecular weights: tannin 1100, rubber (in benzene) 6500, starch 25,000, silicic acid 49,000.

(iii) The *osmotic pressure* of a colloid is small. For 1 p.c. solutions Pfeffer found:

	P cm. Hg	Mol. wt. calc.
Cane sugar - -	47	[342]
Dextrin - - -	16·5	975
Gum arabic - -	7·2	2230

(The mol. wts. are calculated by comparison with cane sugar, *e.g.* $47 \times 342/16{\cdot}5 = 975$.)

Linebarger (1892) measured the osmotic pressure of colloidal tungstic acid, using a parchment paper membrane, and calculated the mol. wt. 1720, $(H_2WO_4)_7$, having a mol. wt. of 1750.

(iv) The *rate of diffusion* of a dissolved substance appears to be inversely proportional to the square-root of the molecular weight. By this method Herzog (1908) found the molecular weight of albumin to be 17,000, whilst Sabanajeff and Alexandroff found 34,000 by the freezing point method and Svedberg the same value by the ultracentrifuge.

(v) The *ultracentrifuge* is a centrifuge rotating at very high speeds (the force being a million times that of gravity), and has been used by Svedberg and others (1925 f.). The sedimentation depends on the molecular weight, as in Perrin's experiment (p. 48). Some colloids are shown to contain more than one kind of particle, and the molecular weights may be very high, *e.g.* 375,000 for casein. The lower values, about 34,500 for albumin and 67,500 for haemoglobin, probably correspond with single molecules.

The ultramicroscope.—Coarse *suspensions* are turbid, settle quickly, and show particles when examined under the microscope. Milk shows globules of fat. Some *colloidal solutions*, however, are clear even under the microscope, but may be distinguished from true solutions by their power of *scattering light*, which shows that they contain very small particles. These are larger than the molecules in true solutions, although molecules scatter light to some

extent, the blue colour of the sky being due to scattering of sunlight by the air molecules.

EXPT. 8.—A few drops of a solution of gum mastic in alcohol are added to water in a glass trough and stirred : the liquid appears clear, but a beam of light from a lantern passed through shows a bright cloudy beam, called a **Tyndall cone** (Fig. 57). The same effect appears in a ray of sunlight passing through dusty air.

FIG. 57.—Tyndall cone, due to the scattering of a beam of light entering at the side, by fine particles suspended in a liquid.

The light scattered by small particles is *polarised*, which distinguishes it from *fluorescence* (shown in this experiment with a few drops of red ink added to the water).

Zsigmondy's **ultramicroscope** consists (Fig. 58) of a microscope with the object-glass dipping into the liquid to be examined contained in a small glass cell. A powerful beam of light is brought to a focus in the liquid by means of a lens. The suspended particles are shown by the scattered light as bright specks.

Microscopic visibility ceases with particles of diameter about $1{\cdot}5 \times 10^{-5}$ cm. or $0{\cdot}15\mu$ (1 *micron* = $1\mu = 0{\cdot}001$ mm.), but the ultramicroscope shows particles down to 5×10^{-7} cm., or $5m\mu$ (1 *millimicron* = $1m\mu = 10^{-6}$ mm.), about one-hundredth the wavelength of visible light.

By the action of phosphorus on gold chloride solution Faraday obtained clear ruby-red colloidal solutions of gold. By counting with the ultramicroscope the number of particles in a known volume (containing a known weight of gold) the diameter of these particles was calculated as $5m\mu$. The pass through filter paper. Still smaller particles of gold, not visible with the ultramicroscope, can act as nuclei or centres of condensation for the formation of ultramicroscopic particles ; the diameter of these nuclei has been estimated as 10^{-7} cm. Zsigmondy distinguished between : **microns**, microscopically visible, diameter 10^{-3} to 10^{-5} cm. (ordinary suspensions), **submicrons**, ultramicroscopically visible, diameter 10^{-5} to 5×10^{-7} cm. (colloidal solutions), and **amicrons**, invisible, but can act as nuclei, diameter 10^{-7} cm. (colloidal solutions).

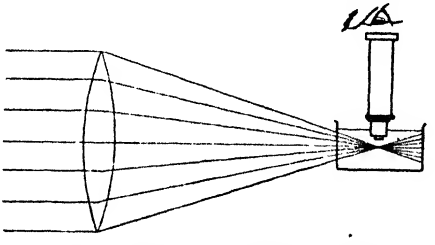


FIG. 58.—Diagram of ultramicroscope.

Gold-leaf is only 10^{-5} cm. thick, and transmits green light from a piece of burning magnesium ribbon held behind a piece of gold-leaf pressed between two sheets of glass.

The *surface* exposed by a given mass is very large for colloidal particles. A cube of 1 cm. side exposes 6 sq. cm. When divided into eight cubes of 0·5

cm. edge the surface is 12 sq. cm., and if the division is carried to the size of colloidal particles the area exposed is of the order of 1 acre. This explains the great catalytic activity of colloidal platinum (p. 682).

The *rate of settling* of spherical particles of radius r cm. and density d g./c.c. in a liquid of density d' g./c.c. and viscosity η c.g.s. units is given by **Stokes's equation**:

$$v = \frac{2r^2g}{9\eta}(d - d') \text{ cm. per sec., } \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(21)$$

where g = acceleration of gravity (981 cm. per sec. per sec.). For a solid of density 2 in water ($d' = 1$, $\eta = 11{\cdot}4 \times 10^{-3}$ at 15°) the velocity for particles of 10^{-4} cm. radius is $1{\cdot}9 \times 10^{-4}$ cm./sec. Such fine particles would not settle, but would be kept suspended by the Brownian movement.

Fogs and smokes.—A suspension of minute bubbles of gas in a liquid is a **froth** or **foam**, and is usually produced by shaking the gas with a liquid of low surface-tension, such as soap solution. A suspension of minute droplets of liquid in a gas, such as is produced by rapidly cooling moist air, is a **mist** or **fog**.

Aitken showed that mists are formed by condensation on minute solid particles (*motes*) of dust or (more probably) salt in the air; if these are partly removed by filtering through cotton-wool, condensation on cooling occurs on the remaining nuclei, producing rain-like drops. If all the nuclei are removed by allowing the air to stand in a vessel with wetted sides, condensation does not occur until the air is cooled much below the normal temperature of mist-formation. C. T. R. Wilson found that electrically charged gaseous ions, produced in dust-free air by α-rays, β-rays, etc., can act as condensation centres (p. 199).

A suspension of fine solid particles in a gas is a *smoke* or *fume*. Coal smoke and tobacco smoke consist mainly of small particles of carbon. Smoke rising from a chimney in clear dry air, or smoke from the glowing end of a cigarette appears blue because the particle sizes are of the order of the wavelength of light. Smoke from a chimney on a damp day, or tobacco smoke blown from the mouth appears greyish-white and opaque because the particles are larger, probably as a result of the condensation of moisture upon them.

In the *Owens dust counter* (1922) a sample of air is taken in a tube lined with moist blotting-paper and by adiabatic expansion through a slit condensation occurs, and the moisture-laden particles stick to a cover-glass below the slit. Their number is counted by a microscope (see R. Whytlaw-Gray and H. S. Patterson, *Smoke*, 1932).

Fog and smoke particles are precipitated by a high tension electric discharge, as found by Sir Oliver Lodge in 1883, and this *electrostatic precipitation* is applied to fumes from smelting, blast, and cement furnaces, and from sulphuric acid concentrators. The *Lodge-Cottrell apparatus* consists of tubes or chambers containing electrodes charged to 75,000 volts. Solid deposited on the tubes is shaken off by tapping with an automatic hammer; liquids flow away.

EXPT. 9.—Electrostatic precipitation is illustrated by the apparatus shown in Fig. 59. The bell-jar rests on a glass plate and the electrodes are copper plates soldered to copper wires fixed in the corks and connected with an induction coil. A small crucible contains cotton-wool moistened with concentrated ammonia solution and hydrogen chloride gas is passed in through the upper tube. A dense fog of ammonium chloride particles forms, but this rapidly settles when the induction coil is operated.

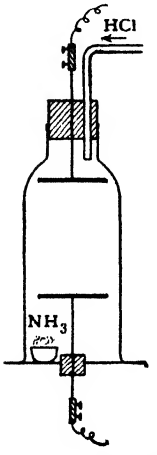


FIG. 59.—Electrostatic precipitation.

Preparation of colloidal solutions.—Colloidal solutions of many *metals* may be prepared by *Bredig's process*, in which small electric arcs are struck between two wires of the metal, *e.g.* platinum or silver, under water. The wires are insulated in glass tubes except for short lengths, and a suitable resistance must be put in series to avoid blowing a fuse. The points under water are repeatedly touched and separated. The metal is evaporated at the high temperature, and very tiny particles of it are dispersed through the water. With platinum and silver, black or brown clouds form round the arc, and dark-coloured colloidal solutions are produced.

Colloidal *silica* is prepared by adding a dilute solution of sodium silicate to excess of dilute hydrochloric acid and dialysing until free from sodium chloride. Colloidal *arsenious sulphide* is made by pouring a solution of arsenious oxide into one of hydrogen sulphide and removing the excess of the latter by bubbling hydrogen through the solution; the solution is clear yellow. Colloidal *ferric hydroxide* is prepared as a clear reddish-brown solution by pouring a few c.c. of 30 p.c. ferric chloride solution into 500 c.c. of boiling distilled water, and dialysing the cooled liquid until free from hydrochloric acid. Colloidal solutions of many metals (*e.g.* colloidal gold) are prepared by reducing a solution of a salt, in presence of a *protective colloid* such as gelatin, by reducing agents such as formaldehyde or hydrazine.

Details on the preparation and properties of colloids are given in special works, *e.g.* Hatschek, *An Introduction to the Physics and Chemistry of Colloids*; Holmes, *Laboratory Manual of Colloid Chemistry*; Michaelis, *Practical Physical and Colloid Chemistry*; Svedberg, *Colloid Chemistry* (Amer. Chem. Soc. Monograph No. 16), 1928; H. R. Kruyt, *Colloids*, 1930; Ostwald and Fischer, *Theoretical and Applied Colloid Chemistry*.

Classification of colloids.—Experiments show that *the transition from true solutions to colloidal solutions is gradual and continuous*, depending on the particle size. Graham's "two worlds" are not so distinct as he thought. A typical colloid such as egg albumin may be obtained in a crystalline form, and crystalline substances such as common salt may be prepared in colloidal form by precipitation in liquids (*e.g.* ether) in which they do not form true solutions. The real factor determining whether a substance forms a colloidal solution or a

true solution is the size of the dispersed particles, and it is more correct to speak of a **colloidal state** than of a "colloidal substance." Even carefully filtered solutions of cane sugar show a slight Tyndall cone, although very much weaker than that obtained with colloidal solutions. Most of the peculiar properties of colloids are due to the large *surface* exposed by the colloid particles (p. 84) and the surface energy located in it (p. 42).

Colloidal particles are not always amorphous. X-ray examination of many colloids, such as colloidal gold with particles $1{\cdot}86 \times 10^{-7}$ cm. diameter, ferric hydroxide, etc., shows that they contain very small crystals.

Colloidal solutions are called **sols**, and the solid forms, which are frequently gelatinous, are called **gels**. A distinction was made between **suspensoids**, in which the colloid particles are solid, and **emulsoids**, in which they are liquid, but a better classification is into **lyophobic** (solvent-repelling) and **lyophilic** (solvent-attracting) **colloids**, respectively.

Lyophobic Colloids (Suspensions)	Lyophilic Colloids (Emulsions)
(i) Non-viscous.	(i) Viscous.
(ii) Not very stable and easily precipitated by electrolytes, the precipitation often being irreversible.	(ii) Fairly stable and not easily precipitated by electrolytes, the precipitation being usually reversible. They "protect" lyophobic colloids from precipitation by electrolytes.
(iii) Non-gelatinising as a rule.	(iii) Gelatinising.
(iv) Particles easily detected by the ultramicroscope.	(iv) Particles not easily detected by the ultramicroscope.
(v) Particles easily show electrophoresis (see below) in electric field.	(v) Particles do not show electrophoresis so markedly.
(vi) Surface tension similar to that of medium (*e.g.* water).	(vi) Surface tension lower than that of medium, hence solutions easily froth on shaking.

Examples of *lyophobic colloids* are: colloidal metals (gold, platinum, etc.), sulphides (*eg.* As_2S_3, Sb_2S_3), hydroxides (ferric and aluminium). Examples of *lyophilic colloids* are: albumin, gelatin.

Electrophoresis.—Suspensoid (lyophobic colloid) particles have electric charges either positive (*e.g.* ferric hydroxide sol) or negative (*e.g.* arsenic sulphide sol), and move in an electric field. This motion called *electrophoresis* (formerly, *cataphoresis*) was discovered by Reuss, of Moscow, in 1807.

Expt. 10.—A colloidal solution of arsenic sulphide (As_2S_3) is made by pouring a boiled, cooled and filtered solution of arsenious oxide in distilled water into a solution of washed hydrogen sulphide in distilled water. The excess of hydrogen sulphide is removed by bubbling a stream of washed hydrogen through the liquid. About 50 c.c. of the yellow solution, with about 5 g. of pure urea dissolved in it to make it denser than water, are carefully run by a pipette into

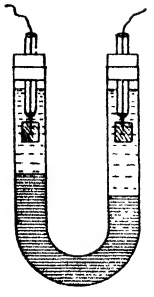


FIG. 60.—Electrophoresis.

the lower part of a U-tube half-filled with distilled water. Platinum electrodes are connected with the D.C. mains. The level of arsenic sulphide falls on one side and rises on the other (Fig. 60).

Lyophilic colloids show some electrophoresis, but the charge on the particles depends largely on the pH (p. 150) of the solution.

Precipitation of colloids by electrolytes.—When an electrolyte is added to a lyophobic (suspensoid) colloidal solution containing charged particles, the colloid is coagulated or precipitated (*e.g.* arsenic sulphide by dilute acid). Colloidal solutions are often protected from precipitation by electrolytes by adding small amounts of lyophilic colloids such as gelatin, which are hence called *protective colloids.*

Colloidal gold with very fine particles is ruby-red, but traces of electrolytes cause the particles to aggregate to coarser particles, and the solution becomes blue and may precipitate. The red solution is much more stable, as Faraday discovered, if a little gelatin is added. The *gold number* of a protective colloid is determined by finding how much of it is required to prevent a standard ruby-gold sol turning blue on addition of sodium chloride. Since gels and lyophilic colloids are insensitive to electrolytes, they probably protect the particles of a lyophobic colloid by forming a coating over them.

If a few drops of sulphuric acid are added to colloidal arsenic sulphide an immediate precipitation of yellow flocks occurs. If the mixture is shaken with paraffin oil, the oil rises to the surface carrying the arsenic sulphide with it. This is an application of *flotation* : arsenic sulphide adheres more strongly to oil than to water.

The precipitating power of an electrolyte depends on the ion of charge opposite to that on the colloid particles. Schulze (1882) and Linder and Picton (*J.C.S.*, 1895, **67**, 63) found that the precipitating power increases rapidly with the valency (electric charge) of the ion. Linder and Picton found that the concentrations of electrolytes in millimols (g. mols./1000) per litre which precipitate an arsenious sulphide sol were : NaCl 51·0, $CaCl_2$ 0·65, $AlCl_3$ 0·09, the effective ions being Na^+, Ca^{++} and Al^{+++}. They also showed that arsenic sulphide precipitated by barium chloride carries down the barium ion (of opposite sign to the sol particles) by adsorption (p. 89), but not the chloride ion.

The amount of adsorption X varies with the concentration of the solution C in the way shown in Fig. 61. Since the coagulation is due to the charge on the ion, if the amount of univalent ion required to precipitate the sol is AB, those of bivalent and tervalent ions will be $A'B' = \frac{1}{2}AB$ and $A''B'' = \frac{1}{3}AB$, and the

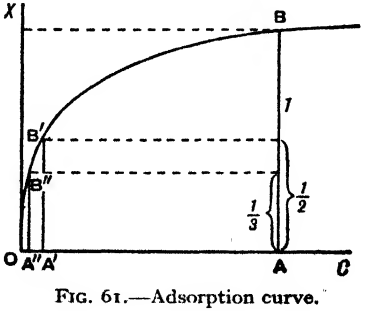


FIG. 61.—Adsorption curve.

curve shows that these are adsorbed from solutions of concentrations OA' and OA'', much smaller than OA.

Lyophilic (*emulsoid*) *colloids* are not easily precipitated by electrolytes; large concentrations are necessary and the effect is of the nature of a "salting-out." It depends on both ions of the salt and on the sign of the charge on the colloid, if it is charged. The order of precipitating power of ions for lyophilic colloids is called the *Hofmeister series* (1888); this depends on the acid, alkaline or neutral reaction of the solution. For anions and albumin in neutral solution the precipitating power is in the order

$$SO_4'' > Cl' > Br' > NO_3' > I' > SCN'.$$

In acid solution the series is reversed. Heavy metal ions have an abnormally high precipitating action.

Solutions of positive (*e.g.* ferric hydroxide) and negative (*e.g.* arsenic sulphide) colloids mutually precipitate one another when mixed in suitable amounts, the opposite electric charges on the particles (which confer stability on the solutions) being neutralised.

Adsorption

In 1777 Scheele, and the Abbé Fontana, independently found that wood charcoal, especially if it has been freed from air and moisture by heating, readily takes up gases.

Expt. 11.—Pieces of recently ignited wood charcoal are passed into a tube of ammonia gas over mercury. The charcoal takes up the gas and the mercury rises and fills the tube. Saussure (1814) found that 1 vol. of charcoal takes up 30 vols. of ammonia gas.

Since the gas is supposed to adhere to the *surface* of the charcoal, including the very large internal surface exposed in the pores, the effect is called *adsorption* to distinguish it from absorption in the bulk of a phase. The surface exposed by 1 mg. of an active charcoal may exceed 1 sq. m. As some penetration into the bulk may also occur, the non-committal word "sorption" has been used.

A very active charcoal is made by heating coconut shell under sand: 1 vol. of this adsorbs at 0° the following volumes of gases at 1 atm. pressure:

Ammonia	171·7	Phosphine	69·1
Cyanogen	107·5	Carbon dioxide	67·7
Nitrous oxide	86·3	Carbon monoxide	21·2
Ethylene	74·7	Oxygen	17·9
Nitric oxide	70·5	Nitrogen	15

The preferential adsorption of ethylene by charcoal has been used to extract it from coal gas. Vapours of volatile liquids are more adsorbed than gases: the volumes of carbon dioxide, ammonia, steam and alcohol vapour adsorbed at 126·5° by charcoal are 16·6, 21·9, 43·8, and 110·8 respectively. Generally speaking, the adsorption increases the nearer the gas or vapour is to its point of liquefaction. McBain found that the amount of gas taken up increases slowly

with time, probably due to a slow penetration of the condensed layer into the interior. At low temperatures the adsorbed amount increases rapidly (Dewar, 1904) :

Gas	He	H_2	A	N_2	O_2	
0°	2	4	12	15	18	volumes at
−185°	15	135	175	155	230	S.T.P.

A bulb of charcoal cooled in liquid air is commonly used to remove gases from evacuated apparatus (see p. 10).

If a Geissler discharge tube containing air at low pressure is connected with a bulb containing charcoal, and this is dipped in liquid hydrogen, the vacuum in the Geissler tube becomes so intense that no discharge will pass even with a powerful coil.

The layer of gas condensed on charcoal is very reactive : chlorine adsorbed on charcoal combines with hydrogen in the dark ; carbon monoxide and chlorine form carbonyl chloride ($COCl_2$) and sulphur dioxide and chlorine form sulphuryl chloride (SO_2Cl_2), when passed over charcoal.

EXPT. 12.—Lower a crucible containing powdered recently ignited charcoal, when just warm, into a dry jar of hydrogen sulphide. After about a minute transfer it to a jar of oxygen. The gases react and the charcoal ignites (Stenhouse, 1855, who invented the charcoal respirator).

Charcoal also adsorbs many *dissolved substances*, *e.g.* metallic salts, organic substances such as alkaloids and colouring matters (Lowitz, 1790), so that it is used to decolorise sugar syrup. Fuller's earth is used in bleaching oils. Charcoal removes fusel oil (amyl alcohol) from crude spirit.

EXPT. 13.—Boil dilute solutions of litmus and indigo with finely powdered animal charcoal, and filter. The filtrates are colourless.

At a given temperature an equilibrium is set up between a gas or dissolved substance and a solid adsorbent such as charcoal or silica gel. The adsorbed amount is proportional to the surface of the adsorbent, and as this includes all the interior pores it is assumed to be proportional to the mass m of adsorbent. If x is the adsorbed amount and p the gas pressure, then at moderate pressures the *adsorption isotherm* equation proposed by Biltz and by Freundlich gives satisfactory results :

$$x/m = kp^{\frac{1}{n}}, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(22)$$

where k and n are constants depending on the nature of the gas and adsorbent and on the temperature. The logarithms of x/m plotted against the logarithms of p give a straight line :

$$\log (x/m) = \frac{1}{n} \log p + \log k. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(23)$$

By measuring the adsorption of gas on plane surfaces such as sheets of mica, Langmuir in 1916 found that it ceases when the surface is covered with

a *unimolecular film* (one molecule thick) of gas, and he deduced the adsorption isotherm :

$$\frac{x}{m} = \frac{ap}{b+p} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(24)$$

where a and b are constants. Thus if $(p \div x/m)$ is plotted against p a straight line is obtained. When p is very small x is proportional to p, and when p is large x is constant, *i.e.* the surface is saturated. This equation agrees well with experiment in many cases (McBain and Britton, *J.A.C.S.*, 1930, **52**, 2198).

For adsorption from a solution of concentration c (at equilibrium) the Biltz-Freundlich equation, which is usually in agreement with experiment, is :

$$x/m = kc^{\frac{1}{n}}. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(25)$$

EXPT. 14.—Solutions of acetic acid of concentrations 0·3, 0·2, 0·1 and 0·05 N are prepared. 50 ml. of each are shaken with 2 g. of active charcoal for about 10 mins., filtered, and 25 ml. titrated with $N/10$ alkali free from carbonate. The equilibrium concentration c g./l. is found in each case and subtracted from the initial concentration c_0. Hence the adsorbed amount is $(c_0 - c) \times 50/1000$. This divided by 2 gives x/m, and by plotting the logarithms of x/m against the logarithms of c a straight line is found :

$$\log (x/m) = \frac{1}{n} \log c + \log k, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(26)$$

from which the values of k and n may be obtained. Acetone, determined by iodimetry, gives more accurate results than acetic acid.*

A theoretical equation deduced by Gibbs (1874) shows that *if a substance decreases the surface tension between the solution and adsorbent it will be positively adsorbed at the interface.* In a surface film the molecules are usually orientated (p. 43), *e.g.* fatty acids R·COOH form a unimolecular film with the carboxyl groups – COOH immersed in the water and the hydrocarbon chain – R projecting from the surface.

Adsorption indicators are used in silver-halogen titrations. When silver nitrate solution is added to a bromide solution a precipitate of silver bromide is formed which is mainly colloidal and is negatively charged owing to adsorption of Br' ion (p. 88). If silver nitrate is added in slight excess the $Ag^{\cdot}$ ion is adsorbed and the precipitate becomes positively charged. If some of the dye *eosin* is present, which is the sodium salt of tetrabromofluorescein, its negative (eosinate) ion is adsorbed on the positive but not on the negative colloid. The end-point is marked by a change of colour of the *precipitate* from pink to deep pink.

* Palmer, *Experimental Physical Chemistry*, Cambridge, 1941, 283.

CHAPTER IV

THERMOCHEMISTRY AND ELECTROCHEMISTRY

Thermochemistry

THERMOCHEMISTRY is the study of heat changes in chemical reactions. The *unit of heat* is the *gram calorie* (g. cal.), which is the heat absorbed when the temperature of 1 g. of water is raised 1° C.* The *kilogram calorie* (or *kilocalorie*) is the corresponding quantity for 1 kg. of water and 1 k. cal. = 1000 g. cal.

Since heat is a form of *energy*, it can be measured in ergs :

$$1 \text{ g. cal.} = 4{\cdot}184 \times 10^7 \text{ ergs},$$

or, as 10^7 ergs is called a *joule*, 1 g. cal. = 4·184 joules. The *kilojoule* (kj.) or 1000 joules is sometimes used as a unit of heat, and 1 k. cal. = 4·184 kj.

Chemical reactions which evolve heat are called *exothermic*, those which absorb heat *endothermic*. It is the standard practice of actual workers, and in nearly all treatises and tables of data, to take heat *evolved* as positive and heat absorbed as negative, but since an evolution of heat corresponds with a decrease of energy the opposite convention is now often used. The heat of reaction refers to the case when the products are finally brought to the same temperature, *e.g.* 18°, as the initial substances.

The heat evolved in the formation of a compound from its elements is equal to the heat absorbed in its decomposition. If the heat evolved is represented by Q a *thermochemical equation* such as

$$C + O_2 = CO_2 + Q$$

means that 12 g. of solid carbon in a specified form (*e.g.* graphite) combine with 32 g. of oxygen gas to form 44 g. of carbon dioxide, and Q g. cal. of heat are evolved, the temperature of the product being finally brought to the temperature of the initial substances, *e.g.* 18°.

When a reaction takes place at *constant volume* and no work is done by a gas expanding against the pressure of the atmosphere, the heat evolved is the decrease of energy of the system, $-\Delta E$. A compound will contain less or more energy than its elements according as heat is evolved in its formation (*exothermic compound*) or is absorbed (*endothermic compound*). The *energy content* of 1 mol of a compound is sometimes called the *intrinsic energy* of the compound. The intrinsic energy contents (or energies) of the elements themselves are arbitrarily taken as zero. It is only energy *changes* which can be measured and these do not depend on the absolute amounts of energy in the elements and compound.

* The specific heat of water varies slightly with temperature, and in accurate work the temperature is specified. If this is 14½° to 15½° the unit is the 15° g. cal., and so on. The unit of heat may also be given in any other energy units, *e.g.* ergs, joules, ft.-lb., etc.

$Cu + S_{(rhombic)} = CuS + 11{,}600$ g. cal. means that 63·57 g. of copper and 32 g. of rhombic sulphur have, together, 11,600 g. cal. of energy more than 95·57 g. of cupric sulphide at the same temperature, and this amount of cupric sulphide has 11,600 g. cal. of energy less than the sum of the energies of the copper and sulphur, this amount of energy being evolved as heat in the reaction.

Heats of reaction.—If E_1 and E_2 are the total energy contents of the initial and final substances in a reaction, the *increase* of energy content due to the reaction is

$$\Delta E = E_2 - E_1 = -Q_v, \quad \ldots\ldots(1)$$

where Q_v is heat evolved at constant volume. This depends only on the starting materials (defining E_1) and the products (defining E_2), and not on how the reaction is carried out.

If the reaction takes place at *constant pressure* and there is a change in volume, work will be done by the system against the atmospheric pressure if there is an increase in volume, and the heat equivalent of this work will be taken from the heat of reaction, so that the heat of reaction evolved at constant pressure Q_p will be less than that at constant volume Q_v by this amount. If there is a decrease in volume (*e.g.* $2H_2 + O_2 = 2H_2O$ (gaseous)), then Q_p is greater than Q_v. The difference $Q_v - Q_p$ is equal to the work *done* against atmospheric pressure. This is significant only when gases take part, as the volume changes of solids and liquids are very small.

If one g. mol. or mol of a gas of volume V is formed at the constant external pressure P, the work done (pressure × increase in volume) is PV. Since V is the molar volume,

$$PV = \mathbf{R}T.$$

Hence if the change is carried out at the constant temperature $T°$ abs. the external work is $\mathbf{R}T$, or approximately $2T$ g. cal. absorbed ($\mathbf{R}$ is nearly 2 g. cal. per 1°).

$\Delta E = E_2 - E_1$ measures the increase of energy and is equal to the heat absorbed ($-Q_v$) in a change at constant volume. In a change at constant pressure P the work done is $P(V_2 - V_1)$, and this amount of heat (in energy units) is absorbed in addition to ΔE. The total heat *absorbed* is

$$\Delta E + P(V_2 - V_1) = (E_2 - E_1) + P(V_2 - V_1).$$

This can be written in the form $(E_2 + PV_2) - (E_1 + PV_1)$, or if we write H for $E + PV$, as $H_2 - H_1 = \Delta H$, the increase in a quantity H, called the *heat content*. If Q_p is the heat of reaction (evolved) at constant pressure,

$$Q_p = -\Delta H. \quad \ldots\ldots(1a)$$

This depends only on the initial and final states (E_1, V_1 and E_2, V_2) at a given constant pressure.

With the convention that heat *absorbed* is positive, which is usual in Thermodynamics and is now often used in Thermochemistry, since ΔE and ΔH are the

increases of energy and heat content, in the new notation the thermochemical equation

$$C + O_2 = CO_2 + 94{,}450 \text{ g. cal.}$$

(reaction at constant pressure) would be written

$$C \text{ (allotropic form specified)} + O_2 \text{ (gas)} = CO_2 \text{ (gas)} ;$$
$$\Delta H = -94{,}450 \text{ g. cal. (for graphite).}$$

The temperature and pressure should also, in strictness, be specified ; if they are not, room temperature (18°) and 1 atm. pressure are understood, and there is then no need to specify the physical states, as these are known under these conditions. Symbols are sometimes used to specify the physical states ; round brackets ( ), square brackets [ ], or no brackets round the symbols mean gases (*e.g.* (H_2O) is steam), solids (*e.g.* $[H_2O]$ is ice) or liquids (*e.g.* H_2O is water). Sometimes the suffixes *g*, *s* and *l* are used for gases, solids and liquids.

Thermochemical quantities can be classified as follows :

(1) **Heat of combustion :** the heat evolved in the combustion of 1 g. atom of an element or 1 g. mol. of a compound in oxygen to give specified products.

(2) **Heat of formation :** the heat change in the formation of 1 g. mol. of a compound from its elements in specified states.

(3) **Heat of reaction :** the heat change in a reaction with the formula weights in grams.

(4) **Heat of neutralisation :** this is usually given for *equivalent* (not molecular) quantities of acid and base in very dilute solution.

(5) **Heat of solution** for 1 g. mol. of a compound in a *very large amount of water*, denoted by Aq. (It varies with concentration, but becomes constant for this case ; otherwise a **heat of dilution** is involved when water is added to a solution). *E.g.* $NH_3 + Aq. = NH_3Aq. + 8400$ g. cal.

In the specification of heat changes, the physical conditions must be stated ; *e.g.* whether the substances reacting are solid, liquid or gaseous ; whether the reaction is between dry substances or in solution in water, and in the latter case the concentration of the solution must be given ; if gases are involved, the temperature and pressure, and whether the reaction is at constant volume or constant pressure, must be stated.

Hess's law.—It is shown above that the heat of reaction, either at constant volume or at constant pressure, depends only on the initial and final states, and does not depend on the intermediate states. This result was found experimentally by Hess in 1840 and is called *Hess's law*. It is usually stated as follows :

If a reaction is carried out in stages the algebraic sum of the amounts of heat evolved in the separate stages is equal to the total evolution of heat when the reaction occurs directly.

Carbon dioxide may be supposed to be produced from carbon (graphite) and oxygen in two stages :

$$(1) \quad C + \tfrac{1}{2}O_2 = CO + q_1 \text{ g. cal.}$$
$$(2) \quad CO + \tfrac{1}{2}O_2 = CO_2 + q_2 \text{ g. cal.}$$

By adding these equations, according to Hess's law, we find

$$(3)\quad C + O_2 = CO_2 + Q \text{ g. cal.}$$
$$q_1 + q_2 = Q;$$
$$\therefore\ q_1 = Q - q_2 = 94{,}450 - 67{,}800 = 26{,}650 \text{ g. cal.}$$

This enables us to find by calculation q_1, the heat of reaction (1) which cannot be found directly by experiment.

Hess's law shows that *a heat of reaction is the algebraic sum of the heats of formation of the products minus the algebraic sum of the heats of formation of the initial substances.* For the compounds on the left of the equation may be supposed first decomposed into the elements, and the substances on the right then formed from these elements.

Thermochemical calculations.—Two examples of the use of Hess's law in solving thermochemical problems are given below (see also Partington and Stratton, *Intermediate Chemical Calculations*, Chap. IX).

(1) From the following heats of combustion calculate the heat of formation of ethylene C_2H_4 from its elements at constant pressure :

$$(1)\quad H_2 + \tfrac{1}{2}O_2 = H_2O + 68{,}370 \text{ g. cal.}$$
$$(2)\quad C + O_2 = CO_2 + 94{,}450 \text{ g. cal.}$$
$$(3)\quad C_2H_4 + 3O_2 = 2CO_2 + 2H_2O + 340{,}000 \text{ g. cal.}$$

The thermochemical equation to be solved for the unknown Q is :

$$(4)\quad 2C + 2H_2 = C_2H_4 + Q \text{ g. cal.}$$

Rearrange equations (1)–(3) so as to give the chemical part of (4) :

From (1) : $2H_2 = 2H_2O - O_2 + 2 \times 68{,}370$ g. cal.
From (2) : $2C = 2CO_2 - 2O_2 + 2 \times 94{,}450$ g. cal.
From (3) : $0 = C_2H_4 + 3O_2 - 2CO_2 - 2H_2O - 340{,}000$ g. cal.
Add : $2C + 2H_2 = C_2H_4 + (136{,}740 + 188{,}900 - 340{,}000)$ g. cal.
$\therefore\ 2C + 2H_2 = C_2H_4 - 14{,}360$ g. cal. (The reaction is endothermic.)

(2) Find the heat of formation of gaseous hydrogen iodide from solid iodine and hydrogen gas from the following heats of reaction, all in k. cal. (for meanings of brackets see above : Aq. is a large amount of water) :

$$(1)\quad (HI) + Aq. = HI\ Aq. + 19{\cdot}20.$$
$$(2)\quad KOH\ Aq. + HI\ Aq. = KI\ Aq. + 13{\cdot}57.$$
$$(3)\quad KI\ Aq. + \tfrac{1}{2}(Cl_2) = \tfrac{1}{2}[I_2] + KCl\ Aq. + 26{\cdot}21.$$
$$(4)\quad KOH\ Aq. + HCl\ Aq. = KCl\ Aq. + 13{\cdot}74.$$
$$(5)\quad \tfrac{1}{2}(H_2) + \tfrac{1}{2}(Cl_2) = (HCl) + 22{\cdot}0.$$
$$(6)\quad (HCl) + Aq. = HCl\ Aq. + 17{\cdot}32.$$

Write (4), (5) and (6) in the reverse order under (1), (2) and (3) and add. This gives :

$$\tfrac{1}{2}(H_2) + \tfrac{1}{2}[I_2] = (HI) - 5{\cdot}92 \text{ k. cal. (absorbed).}$$

The table below gives the heats of formation in k. cal. *evolved* in the formation of 1 g. mol. at room temperature, the physical states being specified by brackets (see above). Sulphur is rhombic and carbon is graphite.

HEATS OF FORMATION

$(H_2) + \frac{1}{2}(O_2) = H_2O$	68·37	$2[P] + \frac{5}{2}(O_2) = [P_2O_5]$	360
$(H_2) + \frac{1}{2}(O_2) = (H_2O)$	57·80	$[C] + (O_2) = (CO_2)$	94·45
$(H_2) + (O_2) = H_2O_2$	45·20	$[C] + \frac{1}{2}(O_2) = (CO)$	26·84
$\frac{1}{2}(H_2) + \frac{1}{2}(Cl_2) = (HCl)$	22·06	$[C] + 2[S] = CS_2$	15·4
$\frac{1}{2}(H_2) + \frac{1}{2}Br_2 = (HBr)$	8·65	$[Na] + \frac{1}{2}(Cl_2) = [NaCl]$	98·3
$\frac{1}{2}(H_2) + \frac{1}{2}[I_2] = (HI)$	−5·91	$[Na] + \frac{1}{2}Br_2 = [NaBr]$	86·7
$(H_2) + [S] = (H_2S)$	5·3	$[Na] + \frac{1}{2}[I_2] = [NaI]$	69·3
$\frac{1}{2}(N_2) + \frac{3}{2}(H_2) = (NH_3)$	11·00	$[Ag] + \frac{1}{2}(Cl_2) = [Ag\ Cl]$	30·3
$[P] + \frac{3}{2}(H_2) = (PH_3)$	2·3	$[Ag] + \frac{1}{2}Br_2 = [Ag\ Br]$	24
$[As] + \frac{3}{2}(H_2) = (AsH_3)$	−44	$[Ag] + \frac{1}{2}[I_2] = [Ag\ I]$	15
$\frac{1}{2}(N_2) + \frac{1}{2}(O_2) = (NO)$	−21·6	$[Ca] + (Cl_2) = [CaCl_2]$	191
$(N_2) + \frac{1}{2}(O_2) = (N_2O)$	−19·7	$[Sr] + (Cl_2) = [SrCl_2]$	198
$[S] + (O_2) = (SO_2)$	71	$[Ba] + (Cl_2) = [BaCl_2]$	205
$[S] + \frac{3}{2}(O_2) = (SO_3)$	93·9	$[Fe] + \frac{3}{2}(Cl_2) = [FeCl_3]$	96·4

Electrochemistry

The subject of electrochemistry dates from the discovery of the so-called *pile* by Volta in 1800. This consisted of a pile of alternate discs of zinc and copper separated by pieces of card moistened with salt solution, and gave an electric current. Nicholson and Carlisle in 1800 decomposed water into hydrogen and oxygen by an electric current, and in 1800 Cruickshank deposited metals from solutions. Wollaston in 1801 showed that frictional and voltaic electricity are the same, the intensity (voltage) being higher for frictional and the quantity being higher for voltaic. Hisinger and Berzelius in 1803 showed that when solutions are decomposed by the current, acids, oxygen and chlorine are deposited at the positive pole, and alkalis, metals and hydrogen at the negative pole.

The first *theory of electrolysis* (as decomposition by an electric current was afterwards called) was put forward by Grotthuss in 1805. He supposed that the molecules become polarised and arrange themselves in chains between the metal poles in the solution (Fig. 62). A pole then attracts an oppositely charged particle, which is deposited, and the other particle takes one of opposite sign from a neighbouring molecule, and so on. The molecules then turn so as to form another chain, and the process is repeated. This theory was taught for many decades.

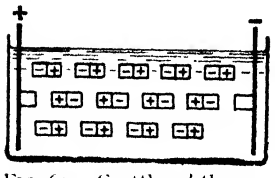


FIG. 62.—Grotthuss' theory.

An important research on electrochemistry was carried out in 1806 by Davy, who in 1807 was able to isolate the alkali metals by electrolysis.

Volta showed that metals become charged on contact, and he arranged them in a series called a *contact series*, those on the left becoming positive

towards those on the right: Zn Pb Sn Fe Cu Pt. Metals, which conduct electricity without undergoing chemical change, also carbon and some metallic sulphides, he called *conductors of the first class*. A liquid such as a salt solution, which is decomposed when the current passes, is a *conductor of the second class*, and if any two metals are connected with each other and a conductor of the second class, a current flows from the more electropositive to the less electropositive metal through the liquid. Ritter in 1799 showed that the order in the contact series is the same as that in which metals precipitate other metals from solutions of salts.

Berzelius in 1811 extended the *electrochemical series* to include non-metals, supposing that atoms had polarities, the *electropositive elements* being on the left and the *electronegative elements* on the right, hydrogen separating two groups of metals:

$$+\text{K Ca Mg Zn Fe Sn Pb} \mid \text{H} \mid \text{Sb Cu Hg Ag Si C N P S I Cl O} -.$$

This agrees with many reactions, *e.g.* the action of water on metals. He also supposed that oxides are either electropositive (*basic oxides*) or electronegative (*acidic oxides*), and that salts are *dualistic compounds* of positive and negative oxides. He formulated sodium oxide as NaO (Na = 46) and sulphur trioxide as SO^3, represented atoms of oxygen by points, and wrote sodium sulphate as $\dot{\text{N}}\text{a}\,\dddot{\text{S}}$.

The Laws of Electrolysis

The *quantitative* laws of electrolysis were announced by Faraday in 1832–3 (*Experimental Researches in Electricity*, partly reprinted in *Everyman's Library*). He adopted some new names which are still in use (Fig. 63). Volta's two kinds of conductors he called (1) *metallic conductors* which conduct without chemical change and are merely heated, and (2) *electrolytic conductors* or *electrolytes*, such as acidulated water, salt solutions and fused alkalis and salts, which are decomposed by the current. The positive and negative poles of the electrolytic cell are the *anode* and *cathode* (Greek *ana* up, *kata* down, and *hodos* a way), and the parts of the electrolyte which seem to move to the electrodes the *ions* (*ion*, neuter participle of *eimi*, go), the negative ion or *anion* going to the positive anode, and the positive *cation* to the negative cathode (Fig. 63). No chemical action appears in the body of the electrolyte, but only at the electrodes; this was explained by the Grotthuss theory, a form of which Faraday adopted.

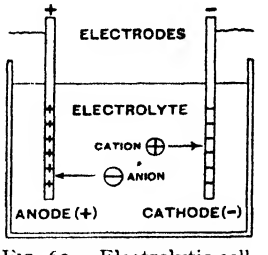


FIG. 63.—Electrolytic cell.

In 1832 Faraday discovered the **first law of electrolysis**: *the weight of an ion deposited is proportional to the quantity of electricity which passes.*

Faraday's own statement was: "the chemical action of a current of electricity is in direct proportion to the absolute quantity of electricity which passes."

Since the quantity of electricity is equal to the (constant) current strength multiplied by the time, the first law may be stated in the form : *the weight of an ion deposited in a given time is proportional to the current strength.*

The quantity of electricity which passes round a circuit is measured in *coulombs* and the current strength in *amperes* ; 1 ampere passing for 1 second conveys 1 coulomb.

In 1833 Faraday discovered the **second law of electrolysis** : *the weights of ions deposited by the same quantity of electricity are in the ratio of their chemical equivalents.* This result also holds for the weights deposited by the same current in a given time.

Faraday's own statement was : " for a constant quantity of electricity . . . the amount of electrochemical action is . . . always equivalent to a standard chemical effect founded upon ordinary chemical affinity."

Faraday compared the quantities of electricity passing through electrolytic cells by measuring the volume of detonating gas ($2H_2 + O_2$) set free from platinum electrodes in acidulated water in a *water voltameter* (Fig. 64) (or *water coulometer*, as it measures coulombs) in series, *i.e.* by making use of his first law. Metal coulometers are now used.

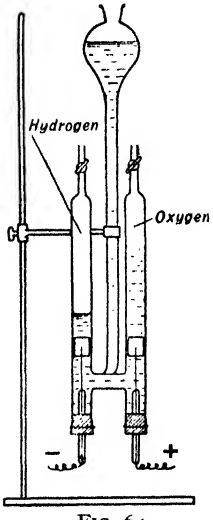


FIG. 64.
Water coulometer.

The *copper coulometer* (Fig. 65) has two sheet copper anodes *A* and *C* hanging from a bent copper rod *DEFG* supported by wooden strips, and a weighed thin sheet copper cathode *B* supported from the copper rod *KL*. The electrolyte is copper sulphate solution containing sulphuric acid (a little alcohol is sometimes added). A current of not more than $\frac{1}{60}$ amp. per sq. cm. of cathode is used.

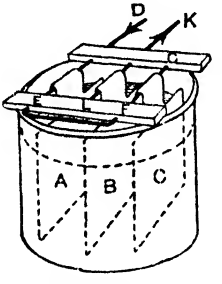


FIG. 65.
Copper coulometer.

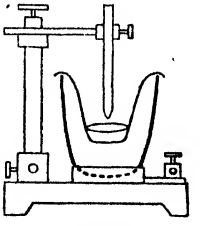


FIG. 66.
Silver coulometer.

The *silver coulometer* (Fig. 66) is a weighed platinum crucible supported on a brass stand and serving as the cathode, and an anode of pure silver rod supported from a brass clamp and wrapped in filter paper, or with a small glass dish below to catch pieces of anode which may fall off. The electrolyte is pure silver nitrate solution.

After the experiment the copper cathode, or the platinum crucible on which the silver deposits, is washed with water and alcohol, dried, and weighed.

The weight of an ion deposited by 1 coulomb is called its *electrochemical equivalent*; for silver this is 0·001118 g., hence the charge required to deposit 1 g. equivalent of any ion (by the second law of electrolysis) is equal to 107·88/0·001118 = 96,494, or very nearly 96,500, coulombs. This is called a *faraday* and denoted by **F** (not to be confused with unit of capacity, the farad). The first and second laws of electrolysis may be summarised together in the statement: 96,500 *coulombs deposit one g. equivalent of an ion in electrolysis.*

The first law may be tested with a coulometer in experiments in which the same current is passed for a given time and for twice that time, when the volumes of gas evolved, or the weights of copper or silver deposited, are in the ratio 1 : 2. In testing the second law, the same current is passed through a water, a copper and a silver coulometer in series, when the weights of hydrogen, oxygen, copper and silver deposited will be in the ratio of the chemical equivalents, 1·008, 8, 31·8, 107·88.

Faraday in 1834 found that *fused salts* obey the laws of electrolysis. Fused stannous chloride gave tin at the cathode and at the anode stannic chloride, formed from the liberated chlorine and the stannous chloride. When 3·85 cu. in. of detonating gas were liberated in the water voltameter (he does not give the temperature and pressure) 3·2 grains of tin were deposited, giving the equivalent 57·9 (instead of 59). Fused lead chloride with a carbon anode was also used, but fused silver chloride gave trouble because the silver crystals (with a high melting point) grew across and short-circuited the electrodes.

Theories of Electrolysis

The Grotthuss theory was long used to explain the mechanism of electrolysis. Berzelius, and also Faraday, thought the ions of a salt were the acidic and basic oxides, but there was a difficulty that in electrolysis not only were acid and base liberated, but also oxygen and hydrogen from the water, so that the current seemed to deposit twice as many equivalents as it should according to Faraday's second law. This was explained by Daniell in 1840. He adopted Davy's theory of salts (1813) in which they were regarded as compounds of metals and acid radicals instead of basic and acidic oxides, sodium sulphate being Na_2SO_4 instead of $Na_2O{\cdot}SO_3$. The current deposits the two radicals in a *primary reaction*, to which the laws of electrolysis apply, and the radicals then decompose the water by *secondary reactions*, not requiring any current, forming acid and base and liberating oxygen and hydrogen:

(1) *Primary reaction*: $Na_2SO_4 = 2Na + SO_4$.

(2) *Secondary reactions*: $2Na + 2H_2O = 2NaOH + H_2$ at the cathode,
$SO_4 + H_2O = H_2SO_4 + \frac{1}{2}O_2$ at the anode.

Since any E.M.F., however small, produces an ionic current in a solution if the opposing E.M.F. of polarisation at the electrodes is absent, no work is spent in decomposing the molecules of an electrolyte into ions. Williamson in 1850 supposed that there is a continual exchange between the atoms or radicals of different molecules of the electrolyte, and during the exchange they are free.

Clausius in 1857 also assumed that the molecules break up spontaneously to a very slight extent into free ions, and the action of the current is to guide these to the electrodes, more ions being formed when these are deposited.

To explain the anomalous results for the freezing and boiling points of solutions of electrolytes (p. 80) Arrhenius in 1887 (see *Alembic Club Reprint* No. 19) supposed that *nearly all the molecules of an electrolyte may be broken up by electrolytic dissociation* (or *ionisation*) *into electrically charged free ions*, and the same conclusion was simultaneously reached by Planck. Since the solution is electrically neutral, the positive and negative charges of the ions must be equal. The charges are usually denoted by points for positive and dashes for negative charges: $Na^{\cdot}$, $Cu^{\cdot\cdot}$, $Fe^{\cdot\cdot\cdot}$, Cl', SO_4'', $Fe(CN)_6'''$, etc.

Since *a current in an electrolyte is carried only by the moving ions*, the weights of these carried to and deposited on the electrodes in a given time are proportional to the current strength. This is equivalent to Faraday's first law.

The second law is explained by assuming that *the electric charge on an ion is the same for all ions of the same valency and is proportional to the valency*. When one faraday **F** passes round the circuit it carries amounts of the ions equal to their atomic or molecular weights divided by their valencies, *i.e.* their chemical equivalents, and deposits them on the electrodes.

When the ions reach the electrodes of opposite sign their charges are neutralised and they deposit as uncharged atoms or radicals, which may then react with water, *e.g.* $2Na^{\cdot}$ and SO_4'' give $2Na$ and SO_4, which react as explained above. From NaCl the chlorine atoms form Cl_2 molecules.

The electron.—Faraday in 1833 said that his second law would be explained if "the atoms of bodies which are equivalents to each other in their ordinary chemical action have equal quantities of electricity associated with them," but he explained that he believed neither in atoms nor in such isolated electric charges. He realised that the ionic charges would be very large; the electricity in a violent flash of lightning would barely decompose a single drop of water.

The idea of a unit ionic charge was revived by Maxwell in 1873, with some reserve, and in 1874, in a paper read to the British Association but not published until 1881, G. Johnstone Stoney calculated the unit ionic charge, afterwards called an *electron*. Helmholtz in 1881 (*J.C.S.*, 1881, **39**, 277: "On the modern development of Faraday's conception of electricity," reprinted in *C.S. Faraday Lectures*, 1928, 12), said that: "if we accept the hypothesis that elementary substances are composed of atoms, we cannot avoid concluding that electricity, positive as well as negative, is divided into definite elementary portions, which behave like atoms of electricity." The free negative electron was discovered by J. J. Thomson in cathode rays in 1895 (p. 184); the positive electron (which has little importance as compared with the negative) was not discovered until 1932 (p. 185). When the name "electron" is used the negative electron (denoted by **e**) is meant.

In electrolysis we suppose that the positive and negative ions move through the solution and arrive at the electrodes of opposite sign. In the metal part of the circuit the free negative electrons move as a current. Negative ions give up one or more electrons to the anode, and at the same time positive ions take

up electrons from the cathode. The uncharged particles are deposited on the electrodes. *E.g.* with copper sulphate, the reaction $SO_4'' = SO_4 + 2e$ occurs at the anode, two electrons move through the connecting wire, and the reaction $Cu'' + 2e = Cu$ occurs at the cathode.

A *positive ion* or *cation* is an atom or radical which has lost a number of electrons equal to its valency: $Na = Na^{\cdot} + e$; $Cu = Cu'' + 2e$. A *negative ion* or *anion* is an atom or radical which has gained a number of electrons equal to its valency: $Cl + e = Cl'$, $SO_4 + 2e = SO_4''$.

From the examples:

$$Fe'' \text{ (ferrous)} \rightleftharpoons Fe'''\text{(ferric)} + e,$$
$$Fe(CN)_6'''' \text{ (ferrocyanide)} \rightleftharpoons Fe(CN)_6''' \text{ (ferricyanide)} + e,$$

we see that *oxidation* corresponds with increase of positive ionic charge or loss of electrons, *reduction* with increase of negative ionic charge or gain of electrons, decrease of positive charge being equivalent to increase of negative charge, and vice versa. In oxidation and reduction reactions these processes occur together and the sum of the ionic charges is the same before and after the reaction:

$$2Fe'' + Cl_2 = 2Fe''' + 2Cl'.$$

Cases where addition of oxygen and change of charge occur together are more complicated; the ion $V^{IV}O''$ is oxidised to the ion $V^{V}O_2^{\cdot}$, although the positive charge decreases. In such cases the valency of an atom (*e.g.* V) always increases in oxidation.

Classes of Electrolytes

Electrolytes which are largely ionised in solution are called *strong electrolytes*, those which are only slightly ionised are called *weak electrolytes*. The following table gives the *degree of ionisation* α as determined by the conductivity in $N/10$ solutions; although the results for strong electrolytes have been modified by modern theory (p. 110) the general picture given by the table is still significant.

Acids		Salts	
Hydrochloric ($H^{\cdot}$, Cl')	0·92	Potassium chloride ($K^{\cdot}$, Cl')	0·86
Nitric ($H^{\cdot}$, NO_3')	0·92	Sodium chloride ($Na^{\cdot}$, Cl')	0·85
Sulphuric ($H^{\cdot}$, HSO_4')	0·61	Potassium nitrate ($K^{\cdot}$, NO_3')	0·83
Phosphoric ($H^{\cdot}$, H_2PO_4')	0·28	Silver nitrate ($Ag^{\cdot}$, NO_3')	0·82
Hydrofluoric ($H^{\cdot}$, F')	0·085	Sodium acetate ($Na^{\cdot}$, CH_3COO')	0·80
Acetic ($H^{\cdot}$, CH_3COO')	0·013	Barium chloride (Ba'', $2Cl'$)	0·75
Carbonic ($H^{\cdot}$, HCO_3')	0·0017	Potassium sulphate ($2K^{\cdot}$, SO_4'')	0·73
Hydrosulphuric ($H^{\cdot}$, HS')	0·0007	Sodium carbonate ($2Na^{\cdot}$, CO_3'')	0·70
Boric ($H^{\cdot}$, H_2BO_3')	0·0001	Zinc sulphate (Zn'', SO_4'')	0·40
Hydrocyanic ($H^{\cdot}$, CN')	0·0001	Copper sulphate (Cu'', SO_4'')	0·39
Bases		Mercuric chloride (Hg'', $2Cl'$)	< 0·01
Sodium hydroxide ($Na^{\cdot}$, OH')	0·91	Mercuric cyanide (Hg'', $2CN'$)	very small
Potassium hydroxide ($K^{\cdot}$, OH')	0·91		
Barium hydroxide (Ba'', $2OH'$)	0·81		
Ammonium hydroxide ($NH_4^{\cdot}$, OH')	0·013		

Strengths of acids.—It is seen from the table above that acids vary considerably in strength, some being very strong (hydrochloric and nitric), others of intermediate strength (sulphuric and phosphoric), and some very weak (acetic and carbonic). The *strength* of an acid as here understood is its degree of dissociation in solution in water, and may not correspond with other less well-defined properties, *e.g.* its corrosiveness or even its power of neutralising peculiar bases such as some organic compounds. The strengths also vary with the solvent.

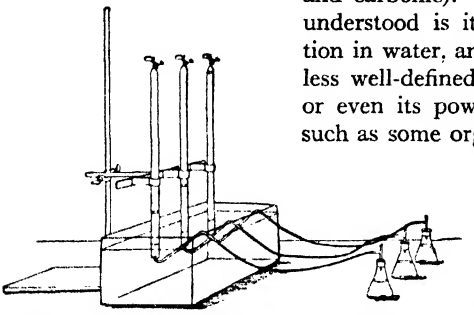


FIG. 67.—Rates of evolution of hydrogen by zinc from different acids.

There are some interesting experiments illustrating the varying strengths of acids. The first concerns the *rate of solution of metals* with liberation of hydrogen, an old method later discredited and now again restored.

EXPT. 1.—Arrange three flasks with delivery tubes Fig. 67). In each place 5 g. of zinc, and pour in 50 c.c. of solutions of hydrochloric (36·5 g. per litre), sulphuric (49 g. per litre), and acetic (60 g. per litre) acids, which contain 1 g. of acidic hydrogen per litre. Add 1 c.c. of dilute copper sulphate to each and after a minute fit the corks and observe the rate of collection of gas. The "strong" acids (hydrochloric and sulphuric) react much more rapidly than the "weak" (acetic), and hydrochloric acid more rapidly than sulphuric.

Since acids in solution owe their acidic properties to the hydrogen ion, their relative strengths may be compared by measuring the relative ionisations in solutions containing equivalent weights in identical volumes. The ionisation runs parallel to the *conductivity*. The hydrogen ion is so much faster than any acid anion (see p. 108) that it carries most of the current, and the relative conductivities of acids are *approximately* proportional to the ionisations.

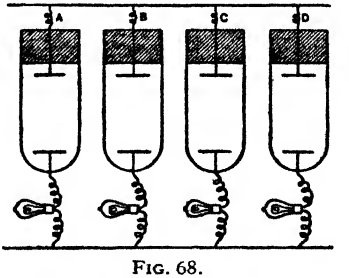


FIG. 68.
Comparison of conductivities.

EXPT. 2.—Distilled water and $N/50$ solutions of acetic, sulphuric and hydrochloric acids are poured into four glass tubes, fitted with copper electrodes (Fig. 68) the same distance apart. A carbon-filament lamp is in series with each tube. The tubes are connected in parallel with the mains. The lamps in circuit with water and acetic acid remain dark, since the conductivities are very small. The lamps connected with the hydrochloric and sulphuric acids light up, but the former is brighter. The order of conductivities of the three acids is

$$HCl > H_2SO_4 > CH_3 \cdot CO_2H,$$

which is the same order as found by the first method.

It should be noted that polybasic acids (dibasic H_2SO_4, tribasic H_3PO_4, etc.) usually ionise in stages, and the first stage of ionisation is greater than the second or third. Sulphuric acid is largely ionised into $H^{\cdot}$ and HSO_4' :

$$H_2SO_4 \rightleftharpoons H^{\cdot} + HSO_4',$$

but the second stage of ionisation into SO_4'' :

$$HSO_4' \rightleftharpoons H^{\cdot} + SO_4''$$

is small except at high dilutions. In the case of phosphoric acid :

$$H_3PO_4 \rightleftharpoons H^{\cdot} + H_2PO_4',$$
$$H_2PO_4' \rightleftharpoons H^{\cdot} + HPO_4'',$$
$$HPO_4'' \rightleftharpoons H^{\cdot} + PO_4''',$$

the third stage is so slight that the PO_4''' ion from Na_3PO_4 takes up hydrogen ion from water to form HPO_4'' and leaves the solution alkaline owing to the OH' ion from the water (*hydrolysis*) :

$$PO_4''' + (H^{\cdot} + OH') \rightleftharpoons HPO_4'' + OH'.$$

Conductivity of Electrolytes

The *specific resistance* or *resistivity* ρ of a metal or electrolyte is the resistance in ohms of a centimetre cube of the material. In the case of a solution ρ is the resistance of the liquid between two electrodes 1 sq. cm. in area and 1 cm. apart. The reciprocal of the specific resistance or resistivity is the *specific conductance* or *conductivity* $\kappa = 1/\rho$, measured in reciprocal ohms, ohm^{-1} (sometimes called " mhos "). By **Ohm's law** κ is equal to the current in amperes between the given electrodes when these differ in potential by 1 volt, or the current in amperes for a potential gradient of 1 volt per cm.

The conductance of a cylinder of material of length l cm. and cross-section s sq. cm. and resistance R ohms is

$$\frac{1}{R} = \frac{\kappa s}{l} \text{ ohm}^{-1}. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2)$$

Since s has the dimensions $(cm.)^2$ and l cm., the dimensions of κ are ohm^{-1} $cm.^{-1}$

$$\kappa = \frac{1}{R}\frac{l}{s}. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(3)$$

When a solution of a partly ionised electrolyte is diluted the conductivity κ decreases because there are fewer ions per c.c., but the degree of ionisation α increases with dilution, since more undissociated molecules ionise.

Let a volume ϕ c.c. of solution containing 1 gram equivalent of electrolyte be poured into a cell with parallel electrodes of any size which are 1 cm. apart (Fig. 69). The current in amperes passing when the potential difference

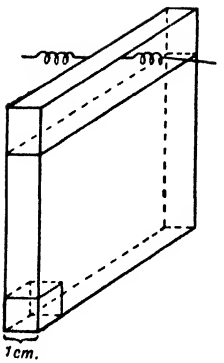


FIG. 69.—Equivalent conductivity.

between the electrodes is 1 volt is defined as the *equivalent conductivity* λ. Since the solution contains ϕ unit cubes in parallel between the electrodes, the current is ϕ times the conductivity κ, hence :

$$\lambda = \phi\kappa. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(4)$$

If η is the concentration in g. *equiv.* per c.c.,

$$\eta = 1/\phi\,; \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(5)$$

$$\therefore\ \lambda = \kappa/\eta. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(6)$$

As the volume ϕ containing 1 g. equiv. increases λ increases and approaches a constant *limiting value* λ_∞ called the *equivalent conductivity at infinite dilution.* Since the concentration then approaches zero, λ_∞ is also denoted by λ_0, the equivalent conductivity at zero concentration.* The dimensions of λ are those of κ multiplied by $(\text{cm.})^3$, *i.e.* $\text{ohm}^{-1}\ \text{cm.}^2$. (The capital letter Λ is now often used instead of λ.)

Determination of conductivity.—In order to eliminate polarisation (p. 122) Kohlrausch (1868) used an alternating current of high frequency, such as is obtained from an induction coil, and increased the surface of the platinum foil electrodes by covering them with platinum black deposited electrolytically from a solution of platinic chloride containing a trace of lead acetate. In this way the polarising effect due to the deposition of ions by the current flowing for an instant in one direction is practically neutralised by the current flowing in the opposite direction for an equal very small interval of time.

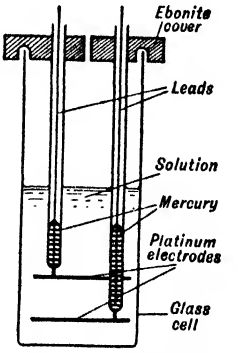


FIG. 70.—Conductivity cell.

The electrolyte is contained in a *conductivity cell* such as that shown in Fig. 70, with parallel platinised electrodes carrying platinum wires welded to them and sealed into glass tubes with mercury contacts and fixed into an ebonite lid. The cell is immersed in a thermostat at 18° or 25°. The cell r is connected with a resistance box R (Fig. 71) and a metre bridge wire.

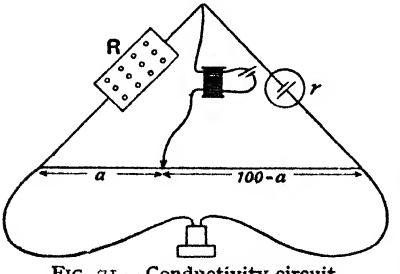


FIG. 71.—Conductivity circuit.

The induction coil is connected with R and r on one side and with a sliding contact on the bridge wire on the other. A telephone connected with the ends of the bridge wire serves to detect an alternating current. The contact is placed near the middle of the wire and plugs taken from the resistance box until the

* This is a *limiting value* of λ, since the *actual* value of κ for $\eta = 0$ is that of the pure solvent.

sound in the telephone is appreciably reduced, the final adjustment being made with the sliding contact until the sound is reduced to a minimum. The bridge is then balanced. It may be necessary to insert a variable condenser in parallel with the resistance box to compensate for the capacity of the cell. Since Ohm's law has been proved experimentally to apply to electrolytes the resistance r of the cell is given by the Wheatstone's bridge formula :

$$R/r = a/(100 - a),$$

where a is the bridge contact reading in cm. and R is the resistance of the box. Hence

$$\frac{1}{r} = \frac{1}{R} \cdot \frac{a}{100 - a}.$$

Since the dimensions of the cell are not easily measured, $1/r$ is connected with the conductivity κ (p. 103) by using a standard electrolyte in the cell. This is normal potassium chloride (74·555 g. KCl, weighed in air, per lit.) for which κ at 18° is 0·09822 (Kohlrausch ; see Jones and Bradshaw, *J.A.C.S.*, 1933, **55**, 1780). If the resistance of the cell is now r' ohms, then $C/r' = 0{\cdot}09822$, where C is the *cell constant* (corresponding with l/s in (3), p. 103). For any other solution $\kappa = C/r$.

Kohlrausch's law.—The independent motion of the ions assumed in the theory of electrolytic dissociation gives a simple explanation of a result found experimentally by Kohlrausch in 1875, called *Kohlrausch's law*. This states that *the equivalent conductivity of a salt at infinite dilution is the sum of two parts, one depending only on the cation and the other only on the anion* :

$$\lambda_\infty = l_c + l_a, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(7)$$

where l_c and l_a are called the *mobilities* of the ions expressed in equivalent conductivity units (ohm^{-1} cm.^{2}) This is illustrated by the figures for λ_∞ at 18° for four salts, the differences being constant :

$$21{\cdot}1 \left\{ \begin{array}{l} \overset{130{\cdot}0}{\mathrm{KCl}} \quad -3{\cdot}7- \quad \overset{126{\cdot}3}{\mathrm{KNO_3}} \\ \\ \underset{108{\cdot}9}{\mathrm{NaCl}} \quad -3{\cdot}7- \quad \underset{105{\cdot}2}{\mathrm{NaNO_3}} \end{array} \right\} 21{\cdot}1.$$

Clearly, $21{\cdot}1 = l_{K^+} - l_{Na^+}$ and $3{\cdot}7 = l_{Cl'} - l_{NO_3'}$.

In order to calculate the separate values of l_c and l_a use is made of the transport number, determined as explained below.

Ionic Migration

Transport number.—Unequal changes in the amount of salt (not ions separately) round the electrodes during electrolysis were noticed by Gmelin in 1838 and by Daniell and Miller in 1843, but were first explained by Hittorf in 1853 as due to *the unequal speeds of the ions.*

In Fig. 72 the black and white circles represent the cations and anions, in the row *a* before electrolysis and in the row *b* after. The cations move to the

left with a speed u and the anions to the right with a speed v, which in the case illustrated is twice as great as u. The vertical line xy divides the original arrangement into two equal parts.

Before electrolysis there are eight pairs of ions on each side. After electrolysis six equivalents of salt have been decomposed and the unpaired ions deposited.

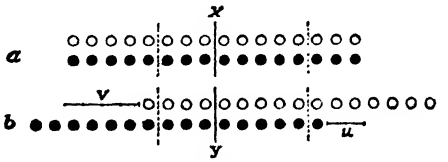


FIG. 72.—Migration of ions.

It is seen that there are four equivalents of salt on the left and six on the right, so that four equivalents of salt have been lost on the left and two on the right.

This example shows that *the losses in neutral salt around the two electrodes are in the ratio of the velocities of the ions migrating away from these electrodes.* The fractions of the total current carried by the cation and anion, respectively, in the above example are one-third and two-thirds; generally they are

$$u/(v+u) \quad \text{and} \quad v/(v+u)$$

where u and v are the velocities of cation and anion. Since the total current λ_∞ is the sum of l_c and l_a, from (7),

$$\lambda_\infty = l_c + l_a,$$

it follows that:

$$\frac{l_c}{\lambda_\infty} = \frac{u}{v+u}, \quad \frac{l_a}{\lambda_\infty} = \frac{v}{v+u}. \quad \text{.....(8)}$$

The *ionic velocities* u and v are in cm. per sec. for a potential gradient of 1 volt per cm. (p. 108).

The fraction of the total current carried by one ion is called its *transport* (in America, *transference*) number n. If n_c, n_a are the transport numbers of cation and anion, then $n_c + n_a = 1$, and

$$l_a/l_c = n_a/n_c = n_a/(1-n_a). \quad \text{.....(9)}$$

It should be noted that the transport number n, unlike the mobility l, is not characteristic of one ion, but varies from salt to salt according to the mobility of the other ion.

In the experimental determination of a transport number by Hittorf's method, the total quantity of electricity passing is determined by a copper or silver coulometer in the circuit and the change in amount of electrolyte round one electrode is measured by analysis of the solution before and after electrolysis.

If W g. or g. equiv of electrolyte correspond with the total charge transfer as measured by the coulometer, and w g. or g. equiv. are *lost* round an electrode,

as found by analysis, the transport number of the ion moving *away from* that electrode is w/W.

An apparatus used for the determination of the transport number for silver nitrate is shown in Fig. 73. The three parts are connected by rubber tubing. The anode *a* and cathode *b* are of thick silver wire cemented into glass tubes and the whole is filled with silver nitrate solution of known concentration and placed in a thermostat. A current of 0·02–0·04 amp. is passed for 1½–3 hours. The experiment must be stopped before any change has occurred in the middle part *c* of the solution, and the current density must not be high enough to cause heating and consequent mixing of the solutions in the different parts by convection. A silver coulometer in series measures the total quantity of electricity passed. After the experiment the screw clips *d*, *d* are closed, the apparatus taken out of the thermostat, and the liquid in the anode compartment removed through *e*, the compartment being washed out with some of the original solution and the total liquid weighed and analysed. The liquid in the U-tube is run out and analysed to make sure that its composition is unchanged. While the apparatus is in the thermostat the rubber tubes are closed by pieces of glass rod *f*.

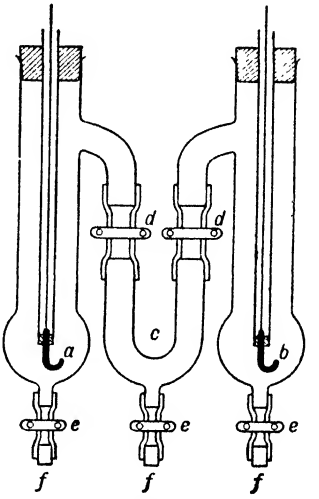


FIG. 73.—Determination of transport number.

An experiment (see Partington and Stratton, *Intermediate Chemical Calculations*, Chap. XI) gave the following results: 1 g. of original solution contained 0·001136 g. Ag or 0·001788 g. $AgNO_3$ and $1 - 0{\cdot}001788 = 0{\cdot}9982$ g. water. After electrolysis 20·09 g. of anode liquid contained 0·03955 g. Ag or 0·06227 g. $AgNO_3$ and $20{\cdot}09 - 0{\cdot}06227 = 20{\cdot}03$ g. water. The original solution contained

$$0{\cdot}001136 \times 20{\cdot}03/0{\cdot}9982 = 0{\cdot}02280 \text{ g. Ag}$$

to 20·03 g. water. ∴ Ag in anode compartment has increased by

$$0{\cdot}03955 - 0{\cdot}02280 = 0{\cdot}01675 \text{ g. Ag.}$$

In the silver coulometer 0·0322 g. Ag deposited and the same weight ($= W$) must have dissolved from the anode, hence the weight of silver which has migrated *away* from the anode is $0{\cdot}0322 - 0{\cdot}01675 = 0{\cdot}01545 = w$. Hence the transport no. of Ag is $0{\cdot}01545/0{\cdot}0322 = 0{\cdot}479$, and that of NO_3 is $1 - 0{\cdot}479 = 0{\cdot}521$.

Mobilities of ions.—From equations (7) and (9) the separate mobilities l_c and l_a can be calculated. *E.g.* for silver nitrate at 18° $\lambda_\infty = 115{\cdot}6 = l_c + l_a$, and $l_a/l_c = 0{\cdot}521/0{\cdot}479 = 1{\cdot}088$. Hence $(115{\cdot}6 - l_c)/l_c = 1{\cdot}088$; ∴ $l_c = 55{\cdot}3$ and $l_a = 115{\cdot}6 - 55{\cdot}3 = 60{\cdot}3$.

The table gives the mobilities in ohm^{-1} cm.^{2} at 18° at infinite dilution and the values of the ionic velocities u and v in cm. per sec. per volt per cm., calculated by equation (11) below. The large mobilities of the hydrogen and hydroxide ions should be noted.

Cations	l_c	$u \times 10^5$	Anions	l_a	$v \times 10^5$
$H^{\cdot}$	315·2	324	OH'	173·8	180
$K^{\cdot}$	64·20	66	Cl'	65·24	68
$NH_4^{\cdot}$	64·3	66	Br'	67·3	70
$Na^{\cdot}$	43·2	45	I'	66·25	69
$Ag^{\cdot}$	53·8	57	NO_3'	61·6	64
$\frac{1}{2}Zn^{\cdot\cdot}$	47·0	49	CH_3COO'	35	37
$\frac{1}{2}Cu^{\cdot\cdot}$	45·9	48	$\frac{1}{2}SO_4''$	68·5	70
$\frac{1}{2}Ba^{\cdot\cdot}$	55·0	57	$\frac{1}{2}CO_3''$	60	63

The value of λ_∞ for a weak acid is found by adding the mobility of the hydrogen ion to the mobility of the anion, *e.g.* for acetic acid $\lambda_\infty = 315{\cdot}2 + 35 = 350{\cdot}2$. The conductivity κ of saturated silver chloride solution at 18°, after suitable correction for the conductivity of the water, is $1{\cdot}24 \times 10^{-6}$ ohm^{-1} cm.$^{-1}$, and the very dilute solution may be considered completely ionised. Now $\lambda = \kappa/\eta$ and $\lambda_\infty = 53{\cdot}8 + 65{\cdot}2 = 119{\cdot}0$. $\therefore\ \eta = 1{\cdot}24 \times 10^{-6}/1{\cdot}190 \times 10^2 = 1{\cdot}04 \times 10^{-8}$ g. equiv. per c.c.

Absolute velocities of ions.—Let a completely ionised solution of 1 g. equiv. of salt be electrolysed with a potential gradient of 1 volt per cm. The ions move with speeds of u and v cm. per sec., and since the total charges on each kind of ion are $+\mathbf{F}$ and $-\mathbf{F}$, respectively, the charges transported per sec. through any section of the solution are $+u\mathbf{F}$ and $-v\mathbf{F}$. Negative charge moving in one direction is equivalent to positive charge moving in the opposite direction, hence the total charge transported per sec. is $u\mathbf{F} + v\mathbf{F}$, which is the same as the current, λ_∞. Hence :

$$\lambda_\infty = \mathbf{F}(u + v). \quad \text{.....(10)}$$

But $\lambda_\infty = l_c + l_a$, and since l_c and u depend on the cation and l_a and v on the anion, it follows that :

$$\left.\begin{aligned} l_c &= \mathbf{F}u \quad \text{and} \quad l_a = \mathbf{F}v, \\ \text{or} \qquad u &= l_c/\mathbf{F} \quad \text{and} \quad v = l_a/\mathbf{F}. \end{aligned}\right\} \quad \text{.....(11)}$$

The units of l_c and l_a are the same as those of λ, ohm^{-1} cm.^{2},

$\therefore\ u = l_c/\mathbf{F} = ohm^{-1}$ cm.^{2}/coulombs, and by Ohm's law,

coulombs = amps. × sec. = volts × sec./ohms = volts × sec. × ohm^{-1} ;

$\therefore\ u = ohm^{-1} \times$ cm.$^2 \times$ ohm × $volt^{-1} \times$ sec.$^{-1}$ = (volt/cm.)$^{-1}$ cm. sec.$^{-1}$.

For 1 g. equiv. of completely ionised electrolyte in the apparatus of Fig. 69 the current is λ_∞. If it is only half ionised and *the velocities of the ions are constant* the current is $\frac{1}{2}\lambda_\infty$, and if a fraction α is ionised it is $\alpha\lambda_\infty$. Hence $\lambda = \alpha\lambda_\infty$ or

$$\alpha = \lambda/\lambda_\infty. \quad \text{.....(12)}$$

This is Arrhenius's method of finding the *degree of dissociation* α.

The velocities of ions in a potential gradient are demonstrated by the following experiment.

EXPT. 3.—The U-tube (Fig. 74) is half-filled with a solution of 0·3 g. of KNO_3 per litre. By connecting a funnel with the tap below, a solution of 0·5 g. of $KMnO_4$ per litre, to each 100 c.c. of which 5 g. of urea have been added to increase its density, is slowly admitted to form a sharp surface of separation between colourless liquid above and purple solution below. A current of 0·3–0·4 amp. is passed between platinum electrodes from D.C. mains. The purple MnO_4' ions move towards the anode and the levels alter as shown. The levels are marked by gummed labels and the change is apparent after 10–15 minutes.

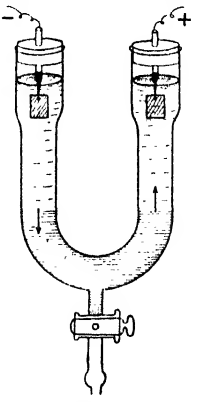


FIG. 74.—Ionic migration.

Lodge in 1886 used a long glass tube containing a jelly made with gelatin, sodium chloride, phenolphthalein and a little alkali, dipping at each end into beakers containing dilute acid and platinum electrodes. On passing the current, hydrogen ions moved through the jelly, decolorising the phenolphthalein, and the velocity was found to be 0·0026 cm. per sec. per volt per cm. Whetham (1893–5) and others used this *moving boundary method*, a very accurate apparatus being that of Longsworth (*J.A.C.S.*, 1930, **52**, 1897).

The ionic velocities are very small, because of the great frictional resistance of the solvent. Kohlrausch calculated that an aggregate force of 1½ million tons would be required to drive the ions of 1 mol of potassium chloride through a solution with a velocity of 1 cm. per sec.

Neutralisation.—Strong acids and bases and most salts are practically completely ionised in solution, but water is only very slightly ionised: $H_2O \rightleftharpoons H^{\cdot} + OH'$. On mixing solutions of an acid and a base the hydrogen and hydroxide ions combine to form water, the other ions remaining free:

$$(H^{\cdot} + Cl') + (Na^{\cdot} + OH') = (Na^{\cdot} + Cl') + H_2O$$

so that the neutralisation reaction is effectively:

$$H^{\cdot} + OH' = H_2O.$$

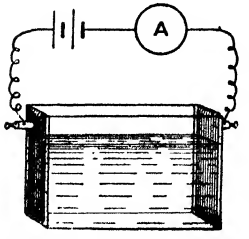


FIG. 75.—Neutralisation.

Since the hydrogen and hydroxide ions have large mobilities (p. 108) the conductivity will fall considerably when they combine.

EXPT. 4.—The rectangular glass trough (Fig. 75) contains two electrodes of sheet copper connected through an ammeter with two accumulators in series. Pour into the cell *N*-caustic soda solution containing urea to increase its density and coloured with phenolphthalein. Float a slice of cork on this solution and add an equal volume of *N*-hydrochloric acid as a layer

above the alkali. Switch on the current and observe the ammeter. This measures the current carried by the ions $Na^{\cdot}$, $H^{\cdot}$, OH', Cl'. Stir the liquids and notice the reduced ammeter reading. The ions $Na^{\cdot}$ and Cl' alone now carry the current.

This principle is used in *conductimetric titration*. The bridge reading for a conductivity cell containing acid (or base) soluion is plotted against c.c. of base (or acid) added from a burette and two lines meeting in a minimum point which gives the equivalence point of the titration are obtained.

Since the reaction of neutralisation of strong acids and bases is always the same : $H^{\cdot} + OH' = H_2O$, the *heat of neutralisation* for equivalent amounts is the same for all and is about 13·7 k. cal. (Mathews and Germann, *J. Phys. Chem.*, 1910, **15**, 73 ; Richards and Rowe, *J.A.C.S.*, 1922, **44**, 684) :

HClAq. + NaOHAq., 13·70,	HNO_3Aq. + NaOHAq., 13·70,
HBrAq. + KOHAq., 13·76,	HClAq. + $\frac{1}{2}Ba(OH)_2$Aq., 13·85.

If the acid or base is weak, part dissociates as the neutralisation proceeds and this causes a heat change. Thus HFAq. + NaOHAq. = NaFAq. + 16·3 k. cal., so that heat is *evolved* in the ionisation of hydrofluoric acid.

If the heat of neutralisation is Q_n, the heat of dissociation of the acid is Q_d, and the degree of dissociation is α, then

$$Q_n = 13{\cdot}7 + (1 - \alpha)Q_d$$

from which Q_d may be calculated.

If an insoluble salt (*e.g.* $BaSO_4$) is precipitated, the heat of neutralisation is also abnormal.

Modern Theory of Electrolytes

In Arrhenius's equation (12) : $\alpha = \lambda/\lambda_\infty$, it is assumed that the ionic velocities (or the mobilities) remain constant and the effect of dilution is to increase the number of ions by electrolytic dissociation of neutral molecules. For many reasons it is now supposed that *strong electrolytes are completely ionised in dilute solutions*, and hence *the change of* λ *on dilution is due to the increase of the ionic velocities* u *and* v (or the *mobilities* l_c and l_a).

Debye and Hückel in 1923 showed that on account of the electrical attractions every selected positive ion is on the average surrounded by more negative than positive ions, and every negative ion by more positive than negative ions. Each *central ion* is thus surrounded by an *ion atmosphere* of equal and opposite charge.

The reduction of equivalent conductivity from λ_∞ at infinite dilution (when the ion atmosphere vanishes) to λ at a given dilution is due to two effects :

(i) the *electrophoretic effect* : the motion of the central ion is retarded by the friction with solvent molecules attached to the ion atmosphere moving in the opposite direction ;

(ii) the *relaxation effect* : the formation and disappearance of the ion atmosphere takes time, and when the central ion moves it leaves part of its atmosphere behind and this, having an opposite charge, drags

it back. The central ion also moves into a place where there is an excess of ions of its own sign, which retards it.

Both effects reduce the velocity of the ion, they disappear at infinite dilution, and they are proportional to the square root of the concentration, $\sqrt{c}$. Hence

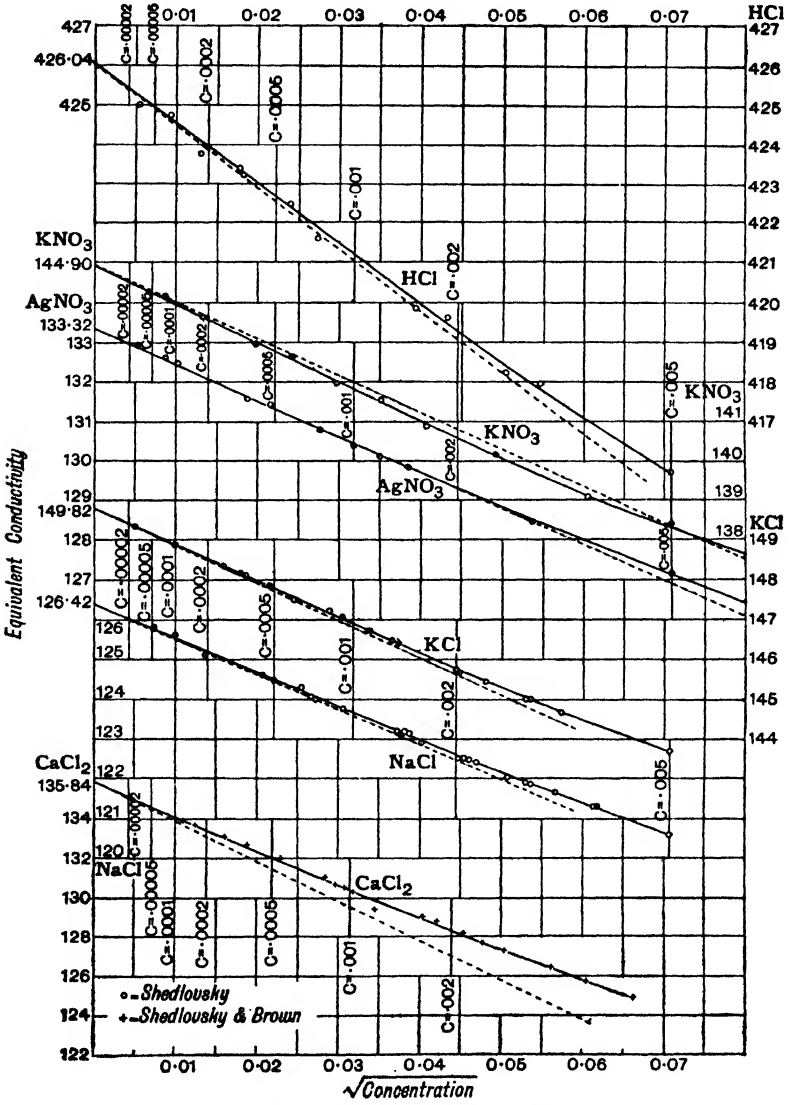


FIG. 76.—Equivalent conductivities of electrolytes.

Reproduced (with modification) from McKenna's "Theoretical Electrochemistry" (Macmillan).

$\lambda = \lambda_\infty - K\sqrt{c}$, where K is a constant for a given solvent (the effects of which depend on its viscosity and dielectric constant) and temperature. This result had been found experimentally long before by Kohlrausch. Onsager in 1926 showed that $K = A + B\lambda_\infty$, where A and B are constants for a given solvent and temperature, hence (writing λ_0 for λ_∞, since $V \to \infty$ as $c \to 0$),

$$\lambda = \lambda_0 - (A + B\lambda_0)\sqrt{c}. \quad \text{.....(13)}$$

For an electrolyte with univalent ions (*e.g.* KCl) in water and c in equiv. per *litre*, this equation becomes :

$$\lambda = \lambda_0 - (59{\cdot}9 + 0{\cdot}228\lambda_0)\sqrt{c} \text{ at } 25°,$$
$$\lambda = \lambda_0 - (50{\cdot}6 + 0{\cdot}225\lambda_0)\sqrt{c} \text{ at } 18°.$$

Onsager's equation holds only at high dilutions and has been empirically modified by Shedlovsky (*J.A.C.S.*, 1932, **54**, 1405 ; 1934, **56**, 1066 ; Jones and Bickford, *ibid.*, 1934, **56**, 602). Onsager's equation can be written :

$$\lambda_0 = \frac{\lambda + A\sqrt{c}}{1 - B\sqrt{c}}, \quad \text{.....(14)}$$

and Shedlovsky added two empirical terms :

$$\lambda_0 = \frac{\lambda + A\sqrt{c}}{1 - B\sqrt{c}} - Cc + Dc \log c, \quad \text{.....(15)}$$

where C and D are constants ; D is usually very small and the last term is then omitted. The equation gives good results and reduces to Onsager's at high dilutions. In Fig. 76 it is seen that the slopes of λ plotted against $\sqrt{c}$ approach the theoretical Onsager slope at high dilutions.

The ratio λ/λ_∞ on the new theory no longer gives the degree of dissociation α for a strong electrolyte (for which $\alpha = 1$), but what is called the *conductivity coefficient* :

$$\lambda/\lambda_\infty = f_c. \quad \text{.....(16)}$$

Even with *weak electrolytes* there is a slight ion interaction, to which the Debye-Hückel theory applies, hence the dissociation constant $\alpha = \lambda/\lambda_\infty$ requires a small correction (Banks, *J.C.S.*, 1931, 3341). If λ_x is the sum of the actual ionic mobilities at a given concentration (assuming complete ionisation) and λ the measured value, then $\alpha = \lambda/\lambda_x$, and λ_x is related to λ_∞ by Onsager's equation with αc instead of c.

Voltaic Cells

An arrangement in which an electric current is produced by a chemical reaction is called a *voltaic cell*. In a simple cell plates of zinc and copper dip into dilute sulphuric acid and are connected by a wire. The zinc atoms dissolve as zinc ions and electrons are set free in the zinc : $Zn = Zn^{\cdot\cdot} + 2\epsilon$. The hydrogen which is liberated when zinc dissolves in dilute acid is now evolved on the copper plate, electrons flowing along the connecting wire and neutralis-

ing hydrogen ions in contact with the copper: $2H^{\cdot} + 2e = H_2$. The reaction $Zn + H_2SO_4 = ZnSO_4 + H_2$, or $Zn + 2H^{\cdot} = Zn^{\cdot\cdot} + H_2$, now occurs in two different places and an electric current is produced.

The Daniell cell (Fig. 77) consists of zinc in dilute sulphuric acid or zinc sulphate solution in a porous pot placed in a copper vessel containing copper sulphate solution. Zinc dissolves as ions: $Zn = Zn^{\cdot\cdot} + 2e$, and the electrons pass along the wire connecting the metals and neutralise the charges on copper ions in contact with the copper vessel: $Cu^{\cdot\cdot} + 2e = Cu$.

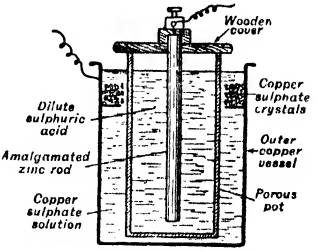


FIG. 77.—Daniell cell.

The true current in the connecting wire is a flow of negative electrons from the zinc to the copper, the conventional "positive current" from the copper to the zinc having no material existence. If a current is passed through the Daniell cell in the opposite direction to the natural current, the changes are reversed, copper dissolving and zinc depositing:

$$Cu = Cu^{\cdot\cdot} + 2e \quad \text{and} \quad Zn^{\cdot\cdot} + 2e = Zn.$$

The Daniell cell is hence called a *reversible cell.* A cell has an *electromotive force* (E.M.F.) measured in volts, and when an opposing E.M.F. very slightly greater than that of a reversible cell is applied, the current direction and the chemical changes in the cell are reversed. The *electrical energy* furnished by a cell is measured by the product of the E.M.F. and the quantity of electricity which flows round the circuit:

$$\textit{energy in joules} = \textit{volts} \times \textit{coulombs}.$$

This energy is capable, theoretically, of being completely converted into useful work by an electric motor and is called *free energy.* In general, free energy is defined as *energy which is completely convertible into work in a reversible change at constant temperature.* The decrease in *free* energy $-\Delta F$ is equal to the work done w, and is usually different from the diminution of *total* energy $-\Delta E$. Thus the electrical work produced by a cell in which a chemical reaction is taking place is not (or only accidentally) equal to the heat of reaction (in joules, p. 92) when the reaction (*e.g.* $Zn + CuSO_4$ Aq. $= Cu + ZnSO_4$ Aq.) takes place directly in a calorimeter without giving a current.

ELECTRODE POTENTIALS

Each pole of a cell has a potential different from that of the earth (conventionally at zero potential), and *the* E.M.F. *of the cell is the difference between the electrode potentials.* How these electrode potentials are set up is explained by Nernst's theory of *electrolytic solution pressure.* This solution pressure is a tendency of a metal to throw off ions into a solution.

A bar of zinc tends to throw zinc ions into a solution of a zinc salt. The metal was uncharged and the ions are positively charged, so that this process

leaves the metal negatively charged : $Zn = Zn'' + 2e$, and the solution positively charged. The *solution pressure* is opposed by the *osmotic pressure* of the zinc ions in the solution, which tends to deposit them on the zinc, and the change soon stops when a mere trace of zinc has dissolved. The zinc ions are attracted by the negative metal (Fig. 78) and form a layer around it. The more zinc ions are in solution, *i.e.* the more concentrated is the zinc salt solution, the greater is their osmotic pressure, the greater their tendency to deposit on the zinc, and the *smaller* is the negative potential of the zinc.

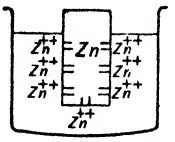


FIG. 78.—Electrical double layer.

If a bar of copper is put into a solution of a copper salt, containing copper ions, the metal has only a very small solution pressure and a trace of copper ions deposit on the metal because of their osmotic pressure and give it a positive charge, leaving the solution negatively charged. The metal then attracts negative ions (*e.g.* SO_4'') from the solution. The more copper ions are in solution, the *greater* is the positive potential of the copper.

If P is the solution pressure of a metal and p the osmotic pressure of its ions in a solution, we see from the above that if P is greater than p (*e.g.* with zinc) the metal becomes negative in the solution ; if P is less than p (*e.g.* with copper) the metal becomes positive in the solution ; whilst if P is equal to p the metal remains uncharged in the solution.

If potassium cyanide is added to the copper sulphate solution in a Daniell cell nearly all the copper ions form the complex ion $Cu(CN)_4'''$ and the direction of the current is reversed, copper becoming the negative pole since, with the low osmotic pressure of copper ions, the metal can throw off ions into the solution.

If we have a bar of zinc in zinc sulphate solution and a bar of copper in copper sulphate solution and connect the two solutions through a porous partition (Fig. 79) we have a Daniell cell. The potential difference between the solutions is small and *the electromotive force of the cell is the algebraic difference between the electrode potentials.* In this case, since one potential is negative, the E.M.F. is the arithmetic sum of the electrode potentials. The negatively charged zinc, with a large solution pressure, tends to throw off positive ions into the solution and hence to drive electrons along a wire connecting the zinc to the copper. The copper has a positive charge and has a greater tendency to take up negative electrons than uncharged copper, hence it reinforces the effect of the zinc. When the metals are connected by a wire a current flows, and zinc dissolves and copper deposits.

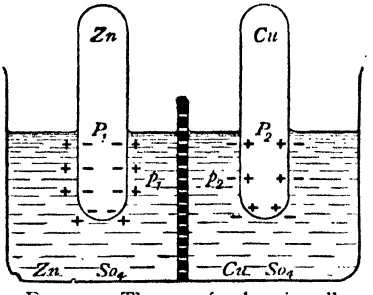


FIG. 79.—Theory of galvanic cell.

Standard electrode potentials.—The potential difference between an electrode and a solution of its ions is called an *absolute electrode potential,* but in

practice the electrode potentials are referred to the potential of a standard electrode, arbitrarily taken as zero. The *standard potential* of a given electrode is then the E.M.F. of a cell composed of that electrode and the standard electrode, the potential difference at the contact of the two solutions round the electrodes being neglected or allowed for.

The *standard electrode*, at Nernst's suggestion, is taken as a *hydrogen electrode*, consisting of a platinised platinum plate surrounded by hydrogen gas at 1 atm. pressure and immersed in an acid solution containing a specified concentration of hydrogen ions (see p. 117). The platinum is negative to the solution. In practice, a secondary standard electrode called the *calomel electrode* (p. 118) is used, consisting of mercury covered with mercurous chloride (calomel) and a normal or decinormal potassium chloride solution, which dissolves a trace of the mercurous chloride : Hg, Hg_2Cl_2, N (or $0{\cdot}1N$)KCl. The mercury is positive, since its solution pressure is so small that the mercurous ions deposit on it. The potential of the N-calomel electrode at 25° referred to the standard hydrogen electrode as zero is +0·2801 volt.

It will be remembered (p. 114) that the electrode potential depends on the ion concentration in the solution, and the standard potentials must refer to some standard concentration for all the ions. Formerly this was $c = 1$ mol per litre, but as it is difficult to find the ion concentration in solutions of strong electrolytes, since the conductivity method fails (p. 110), the electrode potentials are now referred to *unit activity* a of any ion. At very high dilution the activity is equal to the concentration c, and at finite concentrations the ratio a/c, the *activity coefficient*, f, may often be found (p. 166).

The *sign* of an electrode potential varies according to convention ; in Europe it is generally (as in this book) the sign of the charge on the electrode (Zn is − and Cu is +), but in America the opposite convention is often used.

Non-metal electrodes may be made up like the hydrogen electrode, *e.g.* with chlorine gas in contact with platinum in a solution containing chloride ions, when the reaction $Cl_2 + 2e = 2Cl'$ occurs and (since electrons are taken from the platinum) the electrode is positive. The hydrogen electrode is negative because of the reaction $H_2 = 2H^{\cdot} + 2e$, electrons being given to the platinum.

STANDARD ELECTRODE POTENTIALS

K −2·922	Tl −0·33	Ag +0·799
Ca −2·87	Co −0·28	$Hg(Hg_2^{\cdot\cdot})$ +0·80
Mg −2·34	Ni −0·25	Pd +0·82
Al −1·67	$Sn(Sn^{\cdot\cdot})$ −0·136	$Au(Au^{\cdot\cdot\cdot})$ +1·42
Mn −1·05	Pb −0·126	
Zn −0·762	H 0·000	I_2 +0·536
$Fe(Fe^{\cdot\cdot})$ −0·441	Bi +0·226	Br_2 +1·066
Cd −0·402	$Cu(Cu^{\cdot\cdot})$ +0·345	Cl_2 +1·358

The values are in volts at 25° for unit ion activities. A greater negative potential corresponds with a greater tendency to form positive ions, and hence *a metal displaces another from a solution when its electrode potential is more negative*

or algebraically smaller than that of the second metal. Zinc displaces iron, cadmium, copper, silver, etc., and copper displaces silver and mercury. The electrode potential series is thus in the same order as the *electrochemical series* (p. 97). With non-metals, forming negative ions, the order of displacement is reversed, those having a greater *positive* potential (*e.g.* chlorine) displacing those with a smaller (*e.g.* Br_2 and I_2).

Nernst's equation.—The effect of ion concentration on the electrode potential e volts was shown by Nernst to be given by the equation :

$$e = \frac{\mathbf{R}T}{y\mathbf{F}} \ln \frac{p}{P}, \quad \text{.....(17)}$$

where p = osmotic pressure of ion, P = solution pressure of metal, $\mathbf{R}$ = gas constant in electrical units (8·276 joules/1°), T = absolute temperature, $\mathbf{F}$ = 1 faraday = 96,500 coulombs, y is the valency of the ion, and ln denotes the natural logarithm (to the base e). This equation may be written :

$$e = (\mathbf{R}T/y\mathbf{F}) \ln p - (\mathbf{R}T/y\mathbf{F}) \ln P.$$

At a given temperature $(\mathbf{R}T/y\mathbf{F}) \ln P$ is constant for a given metal. The osmotic pressure is given by the equation :

$$pV = \mathbf{R}T \text{ or } p = c\mathbf{R}T,$$

since $1/V = c$ = concentration.

$$\therefore\ e = (\mathbf{R}T/y\mathbf{F}) \ln c - (\mathbf{R}T/y\mathbf{F}) \ln (P/\mathbf{R}T) = (\mathbf{R}T/y\mathbf{F}) \ln c + e_0, \quad \text{.....(18)}$$

where e_0 is the value of e when $c = 1$. More accurately, as explained, the *activity* a must replace the concentration c and e_0 is then somewhat different and is the *standard electrode potential.*

At 18° and with common logarithms ($\ln x = 2{\cdot}3026 \log x$) :

$$e = (0{\cdot}058/y) \log c + e_0. \quad \text{.....(19)}$$

For the zinc and copper electrodes :

$$e_{Zn} = e_{0Zn} + (0{\cdot}058/2) \log [Zn^{\cdot\cdot}] \qquad e_{Cu} = e_{0Cu} + (0{\cdot}058/2) \log [Cu^{\cdot\cdot}]$$
$$= -0{\cdot}76 + 0{\cdot}029 \log [Zn^{\cdot\cdot}]. \qquad = +0{\cdot}34 + 0{\cdot}029 \log [Cu^{\cdot\cdot}].$$

Nernst's equation shows that an electromotive force can be set up between two electrodes of the *same* metal (or other ionising substance) in two solutions of its ions of different concentrations :

$$e = \frac{\mathbf{R}T}{y\mathbf{F}} \ln \frac{p_1}{P} - \frac{\mathbf{R}T}{y\mathbf{F}} \ln \frac{p_2}{P} = \frac{\mathbf{R}T}{y\mathbf{F}} \ln \frac{p_1}{p_2} = \frac{\mathbf{R}T}{y\mathbf{F}} \ln \frac{c_1}{c_2}. \quad \text{.....(20)}$$

This is positive if p_1 is greater than p_2 or c_1 greater than c_2. Hence the metal tends to dissolve in the dilute solution and deposit from the concentrated solution, and if the two pieces of metal are connected a current flows through the cell and the concentrations tend to become equalised. This arrangement is called a *concentration cell.*

EXPT. 5.—A dilute solution of stannous chloride is carefully poured on a concentrated solution (which must not contain much free hydrochloric acid) in a test-tube. A stick of tin is supported in the solutions by a cork (Fig. 80). After a few hours a crystalline deposit of tin forms in the concentrated solution. The positive current flows through the metal from the concentrated to the dilute solution.

FIG. 80.—Experiment on concentration cell.

STANDARD ELECTRODES

Hydrogen electrode.—A convenient form of hydrogen electrode (Fig. 81) is a glass tube *A* open at the lower end, which is perforated about halfway up the wider part, into which is fixed a glass tube *B* carrying the platinised platinum foil electrode *C* (covered with platinum black) by a sealed-in platinum wire touching a mercury contact inside the tube *B*. The electrode dips into dilute sulphuric acid (or other liquid containing hydrogen ions) and a slow stream of pure hydrogen is passed in at *D*, bubbling out below through the perforations.

The platinum electrode, half in the gas and half in the solution, absorbs hydrogen in the atomic form and the hydrogen atoms tend to pass into solution as hydrogen ions, charging the plate negatively: $H = H^{\cdot} + e$. The electrode potential is given by (19), but the hydrogen ion activity $a_{H^{\cdot}}$ is used instead of the concentration, and the standard hydrogen electrode is defined as having zero potential when the hydrogen pressure is 1 atm. and the hydrogen ion activity in the solution is unity: $a_{H^{\cdot}} = 1$. Hence (as $\log 1 = 0$) the constant e_0 is zero and at 18°:

$$e_H = 0{\cdot}058 \log a_{H^{\cdot}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (21)$$

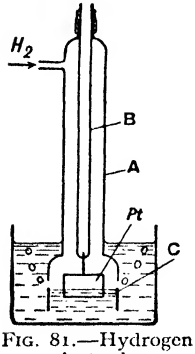


FIG. 81.—Hydrogen electrode.

The hydrogen electrode itself forms only half a cell (a "half element" as it is sometimes called) and it must be connected with the other electrode by bridging the solutions by a glass siphon tube containing a saturated potassium chloride solution plugged at the ends with rolls of filter paper, or else filled with agar jelly made with this solution. This is called a *salt bridge*, and practically eliminates any contact potential between the solutions.

For example, if the electrode potential of copper is determined, a rod of pure copper is immersed in a solution of copper sulphate in a vessel like that shown in Fig. 82, the side tube dipping into a beaker containing saturated potassium chloride solution. From this the salt bridge siphon goes to the acid of the standard hydrogen electrode. If e is the measured E.M.F. of the cell, this is equal to the electrode potential of the copper. As the copper electrode is positive, this is also positive.

The hydrogen ion activity $a_{H^{\cdot}}$ of a solution may be measured by connecting a hydrogen electrode in the solution with a standard hydrogen electrode by

means of a salt bridge. The E.M.F. of the cell at 18° is, from (20) with c replaced by a :

$$e = 0{\cdot}058 \log a_1/a_2 = -0{\cdot}058 \log a_{H\cdot}$$

(since $a_1 = 1$ for the standard electrode).

But $-\log a_{H\cdot}$ is defined as the pH (p. 151) of the solution ;

$$\therefore \text{ pH} = e/0{\cdot}058.$$

At 25° the constant is 0·0591.

Calomel electrode.—The hydrogen electrode is not very easy to use, and it cannot be used with solutions of salts of metals which are reduced by hydrogen. Hence the calomel electrode is generally used as a secondary standard electrode. This may consist of a glass tube with a side tube (Fig. 82) ; it contains some pure mercury (with which contact is made by a platinum wire sealed through a glass tube) covered with solid mercurous chloride (calomel) and is filled with potassium chloride solution, which may be normal (N), decinormal ($N/10$) or saturated, in three types of calomel electrodes. The mercurous ions in the solution deposit on the mercury (which has a very small solution pressure) and give it a positive charge.

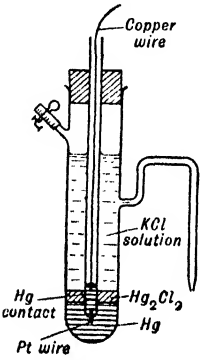


FIG. 82.—Calomel electrode.

If the normal calomel electrode is joined by a salt bridge with a hydrogen electrode the cell is symbolised as

$$\overset{+}{\text{Hg}},\ \text{Hg}_2\text{Cl}_2,\ N\ \text{KCl} \,\|\, \text{sat. KCl} \,\|\, \text{acid } a_{H\cdot},\ \text{H}_2,\ \overset{-}{\text{Pt}},$$

the double lines indicating that the contact potential between the solutions is eliminated. The E.M.F. is the difference between the electrode potentials, or at 25° :

$$\begin{aligned} e &= e_{cal} - e_H \\ &= e_{cal} - 0{\cdot}0591 \log a_{H\cdot} \\ &= e_{cal} + 0{\cdot}0591 \text{ pH} ; \end{aligned}$$

$$\therefore \text{ pH} = (e - e_{cal})/0{\cdot}0591. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (22)$$

The values of e_{cal} in volts referred to the standard hydrogen electrode as zero are : $N/10$ 0·3335, N 0·2801, saturated 0·246.

The calomel electrode may also be used as a half element in measuring the electrode potential of a metal, *e.g.* Cu in $CuSO_4$ solution or Zn in $ZnSO_4$ solution.

An ***electrometric titration*** may be carried out by immersing a hydrogen electrode in the acid solution, connecting the solution with a calomel electrode, and running standard alkali into the acid from a burette. The large change of pH in passing the neutral point is shown by a pronounced inflexion on the curve of E.M.F. plotted against the volume of alkali added.

Quinhydrone electrode.—Biilmann in 1921 showed that the hydrogen electrode can be replaced by an electrode in which a piece of bright platinum dips into an acid solution containing a small quantity of quinhydrone. This is a sparingly soluble compound of equimolecular amounts of quinone $C_6H_4O_2$ (= Q) and hydroquinone $C_6H_4(OH)_2$ (= H_2Q). Owing to the reaction

$$C_6H_4(OH)_2 \rightleftharpoons C_6H_4O_2 + 2H^+ + 2\ominus$$

the quinhydrone is equivalent to a very small pressure of dissolved hydrogen, and the arrangement behaves as a hydrogen electrode. Against the standard hydrogen electrode at 25° it has a potential of 0·700 volt. Since the ratio H_2Q/Q is always 1 (the quinhydrone containing them in equimolecular amounts) the very small hydrogen pressure is constant, from the law of mass action (Chap. V)

$$[H]^2 = K[H_2Q]/[Q] = \text{const.},$$

where K is the equilibrium constant. The hydrogen dissolves in the platinum and exerts a constant solution pressure P, proportional to [H], against hydrogen ions in solution of osmotic pressure p, which may be put proportional to the hydrogen ion activity a_{H^+}. Hence from (17) the electrode potential at 25° is given by :

$$e_Q = \frac{RT}{F} \ln \frac{ka_{H^+}}{[H]} = 0{\cdot}0591 \log a_{H^+} + e_0,$$

where k is a constant and e_0 is also a constant, 0·700. Hence the electrode potential is :

$$e_Q = 0{\cdot}700 + 0{\cdot}0591 \log a_{H^+} = 0{\cdot}700 - 0{\cdot}0591\ \text{pH}.$$

A saturated calomel electrode is generally used as a half element with the quinhydrone electrode, which in this case is positive to the calomel electrode :

$$\overset{+}{\text{Pt}},\ \text{quinhydrone},\ a_{H^+} \parallel \text{sat. KCl},\ Hg_2Cl_2,\ \overset{-}{\text{Hg}},$$

hence the E.M.F. is

$$e = e_Q - e_{cal} = 0{\cdot}700 - 0{\cdot}0591\ \text{pH} - 0{\cdot}246\ ;$$
$$\therefore\ \text{pH} = (0{\cdot}454 - e)/0{\cdot}0591.$$

The quinhydrone electrode does not give good results for pH greater than 6, owing to oxidation, and to appreciable ionisation of hydroquinone as an acid :

$$H_2Q \rightleftharpoons H^+ + HQ' \rightleftharpoons 2H^+ + Q''.$$

The glass electrode.—When glass is in contact with a solution containing hydrogen ions a potential difference arises at the surface which depends on the pH value of the solution. If two solutions are separated by a thin glass membrane, *e.g.* a thin bulb (Fig. 83), a potential difference proportional to the pH difference up to pH = 9 is set up. The inside solution may be N HCl containing some quinhydrone giving

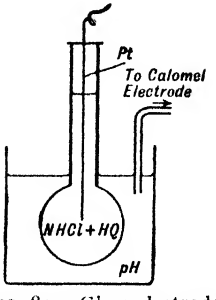


FIG. 83.—Glass electrode.

a constant pH, and a platinum electrode is put in it; the solution of unknown pH is outside and is connected by a salt bridge with a calomel electrode. The electrode is standardised with outside solutions of known pH (see Hughes, *J.C.S.*, 1928, 491).

Oxidation-Reduction Potentials

It has been explained (p. 101) that in reduction an ion gains electrons and in oxidation it loses electrons. A platinum electrode in a solution tends to lose electrons to an ion which can be reduced (*i.e.* an oxidising agent) and the platinum becomes charged positively, while it tends to take up electrons from an ion which can be oxidised (*i.e.* a reducing agent) and becomes charged negatively.

The more easily an ion loses electrons the stronger it is as a reducing agent and the greater is the negative potential of a platinum electrode in its solution, and the more easily the ion gains electrons the stronger it is as an oxidising agent and the greater is the positive potential of a platinum electrode in its solution. The potential between a platinum electrode and a solution thus measures the oxidising or reducing strength of the solution. These potentials are called *oxidation-reduction potentials* (or " redox " potentials).

A ferric salt is reduced by nascent hydrogen :

$$Fe^{\cdot\cdot\cdot} + H = Fe^{\cdot\cdot} + H^{\cdot},$$

and if we suppose the reaction reversible we may postulate a very small concentration of atomic hydrogen in equilibrium with the solution :

$$[H] = K[Fe^{\cdot\cdot}][H^{\cdot}]/[Fe^{\cdot\cdot\cdot}].$$

A platinum plate in a solution containing ferrous and ferric ions may thus be regarded as a hydrogen electrode. The hydrogen dissolves in the metal and exerts a solution pressure P proportional to [H] against the osmotic pressure of hydrogen ions in solution, which is proportional to $[H^{\cdot}]$. Hence in (17) we can replace p/P by const. $\times [H^{\cdot}]/[H]$, *i.e.* by const. $\times [Fe^{\cdot\cdot\cdot}]/K[Fe^{\cdot\cdot}]$. As y (the charge in **F** transferred in the electrode reaction) $= 1$ $(= 3 - 2)$:

$$e = \frac{\mathbf{R}T}{\mathbf{F}} \ln \frac{\text{const.} \times [Fe^{\cdot\cdot\cdot}]}{K[Fe^{\cdot\cdot}]}$$

$$= e_0 + \frac{\mathbf{R}T}{\mathbf{F}} \ln \frac{[Fe^{\cdot\cdot\cdot}]}{[Fe^{\cdot\cdot}]},$$

where e_0 is a constant, the value of e when $[Fe^{\cdot\cdot\cdot}] = [Fe^{\cdot\cdot}]$.

This deduction applies to other cases, and if [Ox] and [Red] are the concentrations of oxidised and reduced forms, corresponding with $[Fe^{\cdot\cdot\cdot}]$ and $[Fe^{\cdot\cdot}]$, and the reversible oxidation-reduction reaction is

$$\text{Red} \rightleftharpoons \text{Ox} + y\mathbf{e},$$

where y electrons are involved, *i.e.* y is the difference in valencies of oxidised and reduced forms of the ion, the oxidation-reduction electrode potential (which

corresponds with the single electrode potential of a metal in a solution of its ions) is given by :

$$e = e_0 + \frac{\mathbf{R}T}{y\mathbf{F}} \ln \frac{[\text{Ox}]}{[\text{Red}]} . \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (23)$$

At 25°
$$e = e_0 + \frac{0{\cdot}0591}{y} \log \frac{[\text{Ox}]}{[\text{Red}]} .$$

e_0 is a constant and the standard state (for which $e = e_0$) is [Ox] = [Red].

The oxidation-reduction electrode must be combined with a standard electrode such as the hydrogen electrode or calomel electrode in order to measure the oxidation-reduction potential. Thus, we could take a solution containing ferrous and ferric sulphates, insert a platinum electrode, and connect the solution by a salt bridge with a normal calomel electrode :

$$\overset{+}{\text{Hg}},\ \text{Hg}_2\text{Cl}_2,\ N\,\text{KCl} \parallel \text{sat. KCl} \parallel \text{Fe}^{\cdot\cdot}, \text{Fe}^{\cdot\cdot\cdot},\ \overset{-}{\text{Pt}}.$$

The E.M.F. will be $e_{\text{cal}} - e_{\text{OR}}$, where e_{OR} is the oxidation-reduction potential, hence the latter may be calculated. By varying the ratio $[\text{Fe}^{\cdot\cdot\cdot}]/[\text{Fe}^{\cdot\cdot}] = [\text{Ox}]/[\text{Red}]$ we can test (23) and calculate e_0, the standard oxidation-reduction potential.

Some values of the standard oxidation-reduction potentials for various reactions are given in the table, the standard being the hydrogen electrode. Since more positive potentials correspond with oxidising, and more negative with reducing agents, the order from the top is that of oxidising power and that from the bottom of reducing power.

OXIDATION-REDUCTION POTENTIALS

Electrode	Electrode Reaction	e_0
$Pb^{\cdot\cdot\cdot\cdot}$, $Pb^{\cdot\cdot}$	$Pb^{\cdot\cdot\cdot\cdot} + 2e = Pb^{\cdot\cdot}$	+ 1·75
$Ce^{\cdot\cdot\cdot\cdot}$, $Ce^{\cdot\cdot\cdot}$	$Ce^{\cdot\cdot\cdot\cdot} + e = Ce^{\cdot\cdot\cdot}$	+ 1·45
MnO_4', $Mn^{\cdot\cdot}$	$MnO_4' + 8H^{\cdot} + 5e = Mn^{\cdot\cdot} + 4H_2O$	+ 1·48
Cl_2, $2Cl'$	$Cl_2 + 2e = 2Cl'$	+ 1·36
Cr_2O_7'', $2Cr^{\cdot\cdot\cdot}$	$Cr_2O_7'' + 14H^{\cdot} + 6e = 2Cr^{\cdot\cdot\cdot} + 7H_2O$	+ 1·3
Br_2, $2Br'$	$Br_2 + 2e = 2Br'$	+ 1·07
$Fe^{\cdot\cdot\cdot}$, $Fe^{\cdot\cdot}$	$Fe^{\cdot\cdot\cdot} + e = Fe^{\cdot\cdot}$	+ 0·75
I_2, $2I'$	$I_2 + 2e = 2I'$	+ 0·54
$Fe(CN)_6'''$, $Fe(CN)_6''''$	$Fe(CN)_6''' + e = Fe(CN)_6''''$	+ 0·49
$Cu^{\cdot\cdot}$, $Cu^{\cdot}$	$Cu^{\cdot\cdot} + Cl' + e = CuCl$	+ 0·46
$Sn^{\cdot\cdot\cdot\cdot}$, $Sn^{\cdot\cdot}$	$Sn^{\cdot\cdot\cdot\cdot} + 2e = Sn^{\cdot\cdot}$	+ 0·2
H_2, $2H^{\cdot}$	$2H^{\cdot} + 2e = H_2$	0·0
$Cr^{\cdot\cdot\cdot}$, $Cr^{\cdot\cdot}$	$Cr^{\cdot\cdot\cdot} + e = Cr^{\cdot\cdot}$	− 0·41

An *oxidation-reduction titration* may be carried out electrometrically with a bright platinum electrode in the solution to be titrated, *e.g.* containing ferrous salt and dilute sulphuric acid, the other electrode being a calomel half-element connected with a salt-bridge. Decinormal dichromate is run in from a burette. Owing to the large change in log ($[\text{Fe}^{\cdot\cdot\cdot}]/[\text{Fe}^{\cdot\cdot}]$) at the equivalence point there

is a large change of potential (about 300 millivolts) at that point, which is easily detected by plotting the measured E.M.F. against ml. of dichromate added.

Oxidation-reduction (redox) *indicators* change colour in an oxidation-reduction reaction. They are usually organic compounds having different colours in oxidised and reduced forms. Diphenylamine in sulphuric acid is used as an internal indicator in the titration of ferrous ion by dichromate, when a blue colour is formed by a drop of dichromate in excess.

Decomposition Potentials

Although the deposition of a g. equiv. of any ion requires the same *quantity* of electricity, 96,500 cmb., the *energy* is different for different ions, and since this is the product of coulombs and volts, the decomposition potentials are different. A Daniell's cell (1·1 volts) will not decompose water, whilst an accumulator (2 volts) will do so.

Since the current passes only when ions are depositing, the *decomposition potential* is determined by immersing bright platinum electrodes in the solution and applying to them a gradually increasing potential difference by means of a potentiometer circuit. A galvanometer included in the electrolytic circuit shows a sudden large increase in current when decomposition sets in.

When the decomposition is reversible the decomposition potential is the algebraic difference of the electrode potentials of the two ions, since the electromotive force of *polarisation* set up by the products of decomposition, acting as a cell, must be overcome before further deposition can occur.

In practice a larger potential than this is required to deposit an ion, especially when hydrogen is liberated, and the excess is called the *overvoltage* of the ion. For hydrogen this is very small on platinised platinum, but is large on amalgamated lead.

The formation of sodium amalgam in the Castner-Kellner alkali cell (p. 773) is possible, although the potential to deposit sodium is much higher than that normally required to deposit hydrogen. Hydrogen has a large overvoltage on mercury, and sodium is deposited instead.

Le Blanc found the following decomposition potentials in volts for the liberation of hydrogen and oxygen from *N* solutions of some acids and bases:

H_2SO_4	1·67	NaOH	1·69
HNO_3	1·69	KOH	1·67
H_3PO_4	1·70	NH_4OH	1·74

The values are all practically equal, hence Le Blanc concluded that the electrode reactions are all the same, viz. the discharge of $H^{\cdot}$ and OH' ions from the water: $2H^{\cdot} + 2e = H_2$, and $2OH' - 2e = H_2O + \frac{1}{2}O_2$. Although the acid anions carry the current to the anode, the OH' ions of the water are actually discharged, leaving $H^{\cdot}$ ions to pair with the anions.

The decomposition potentials of salt solutions which give only hydrogen and oxygen are rather higher than those of the acids and bases :

Na_2SO_4	2·21	$NaNO_3$	2·15
K_2SO_4	2·20	$Ca(NO_3)_2$	2·11
KNO_3	2·17	$Ba(NO_3)_2$	2·25

The reason is that with salts alkali forms round the cathode and acid round the anode, so that hydrogen and oxygen are discharged from alkaline and acid solutions, respectively, which is the reverse of the normal case. In these cases the current is carried by the salt ions, but hydrogen and oxygen are discharged at the electrodes from the hydrogen and hydroxide ions of water, which are more easily deposited :

$$\begin{array}{ccccc} & & + & & - \\ & & \leftarrow SO_4'' & 2Na^{\cdot} \rightarrow & \\ H_2O + \tfrac{1}{2}O_2 \leftarrow & 2OH' & 2H^{\cdot} & 2OH' & 2H^{\cdot} \rightarrow H_2. \end{array}$$

The other ion of the water remains to form acid and alkali with the salt ions which have moved to the electrodes. Thus hydrogen and oxygen are *primary products* of electrolysis, and not secondary products as assumed by Daniell (p. 99).

The decomposition potentials of halogen acids are quite different, since now halogen and not oxygen is deposited :

HCl	1·31	HBr	0·94	HI	0·52

Since copper is deposited with a lower electrode potential than cadmium it is possible to separate practically all the copper from a mixture with an E.M.F. insufficient to deposit any cadmium. When all the copper is deposited the current ceases. If the E.M.F. is then raised the cadmium is deposited. This principle is used in *electroanalysis*. If the concentration of copper ions is made very small by adding a cyanide (which forms a complex ion) a higher potential is required to deposit copper, and if zinc is present the two may be deposited together as the alloy brass.

The products of electrolysis depend on the *current density* at an electrode, this being the current in amperes per sq. cm. of electrode. With a high current density the ions near an electrode which are more easily deposited are thrown out rapidly, and as diffusion is slow other ions with higher deposition potentials may then deposit. Some metals may be deposited along with hydrogen with a high current density, and in sulphuric acid ozone and persulphuric acid are formed, the anodic potential rising.

CHAPTER V

THE LAW OF MASS ACTION

Reversible Reactions

In the early history of chemistry it was assumed that substances closely related to one another (*e.g.* mercury and gold) show the greatest tendency to combine, hence the name **affinity** (from *affinis*, related) was given to the cause of combination. This is true for the miscibility of liquids and metals, but these are not often cases of true chemical combination. Such changes as the neutralisation of acids and alkalis seemed to show, on the contrary, that *dissimilar* substances react most easily, and the electrochemical theory of Berzelius (1811) regarded substances of opposite electrochemical character as most prone to combination.

Mayow (1674) held very clear views on chemical affinity. He refers to the distillation of nitre with sulphuric acid, which displaces the nitric acid, " because the volatile acid . . . has been expelled from the society of the alkaline salt by the more fixed vitriolic acid," thus realising the effect of the *volatility* of a product on a chemical change.

Geoffroy (1718) and Bergman (1775) considered that if a substance A acts on a compound BC, and if A has a stronger affinity or attraction for B than C has, then A will decompose BC *completely*, turning out C and forming AB. Hence tables of affinity were drawn up, giving the order in which substances displace each other either in solution or in the state of fusion.

This theory of *elective affinities* was called into question by Berthollet (1799–1803). He pointed out that the reaction $A + BC = AB + C$ does not always go to completion in one direction according to Bergman's theory. It may take place in the opposite direction and in general is not complete : " in opposing the body A to the combination BC, the combination AB can never take place [completely], but the body B will be divided between the bodies A and C proportionally to the affinity and the quantity of each."

Berthollet made a notable advance by recognising that : (i) chemical reactions are often incomplete and reversible, (ii) the course of a reaction depends on physical conditions, *e.g.* temperature, pressure, the presence of a solvent, etc., (iii) the volatility and insolubility of the products produce important effects, and (iv) the quantity (more correctly, the *concentration*) of a substance can influence a reaction—this was called the *action of mass*.

Unfortunately, since Berthollet regarded solutions as chemical compounds, he believed that compounds can vary in composition, and as this contradicted Proust's experiments on constant proportions and Dalton's atomic theory, Berthollet's other views did not receive adequate recognition.

Berthollet saw that many chemical reactions of the type $A + BC = AB + C$ go on only to a certain point, because the opposed reaction $AB + C = A + BC$

can take place under the *same* conditions and at the same time as the direct reaction. This leads to a **state of equilibrium**, when the two opposing reactions balance each other: $A + BC \rightleftharpoons AB + C$.

Steam is reduced by heated iron giving hydrogen and oxide of iron: $3Fe + 4H_2O = Fe_3O_4 + 4H_2$, and *under the same conditions* oxide of iron is reduced by hydrogen giving iron and steam: $Fe_3O_4 + 4H_2 = 3Fe + 4H_2O$. A state of equilibrium is set up in which as much steam is decomposed as is formed in a given time:

$$3Fe + 4H_2O \rightleftharpoons Fe_3O_4 + 4H_2.$$

Other examples are the decomposition of barium peroxide by heat: $2BaO_2 \rightleftharpoons 2BaO + O_2$, the dissociation of steam by electric sparks: $2H_2O \rightleftharpoons 2H_2 + O_2$, and the formation and decomposition of ammonia by sparks: $N_2 + 3H_2 \rightleftharpoons 2NH_3$.

Dulong in 1813 found that barium sulphate when boiled with successive quantities of potassium carbonate solution is completely converted into barium carbonate; whilst barium carbonate when boiled with successive quantities of potassium sulphate solution is entirely transformed into barium sulphate, and the reaction is therefore reversible: $BaSO_4 + K_2CO_3 \rightleftharpoons BaCO_3 + K_2SO_4$. Both $BaSO_4$ and $BaCO_3$ are slightly soluble and the reactions proceed *in solution.*

Chemical Equilibrium

The equilibrium state.—When hydrogen and iodine vapour are heated together some hydrogen iodide is formed: $H_2 + I_2 = 2HI$, and when hydrogen iodide is heated part of it is decomposed into hydrogen and iodine vapour: $2HI = H_2 + I_2$. In presence of platinum as a catalyst a state of equilibrium is reached, when both reactions proceed at equal speeds: $H_2 + I_2 \rightleftharpoons 2HI$. The same state of equilibrium is reached on heating hydrogen iodide gas for a sufficient time as on heating a mixture of hydrogen and iodine vapour in equivalent proportions, at the same temperature.

This was proved by Lemoine (1877) and by Bodenstein (1894). Either hydrogen iodide or a mixture of equivalent amounts of hydrogen and iodine vapour was heated in sealed bulbs at a constant temperature, *e.g.* in a sulphur vapour bath at 445°, for varying times. Separate bulbs were rapidly cooled and, since the reaction is very slow at room temperature, the content of a bulb gives the composition of the gas before cooling. One tip of the bulb was broken under potassium hydroxide solution and the volume of residual hydrogen found.

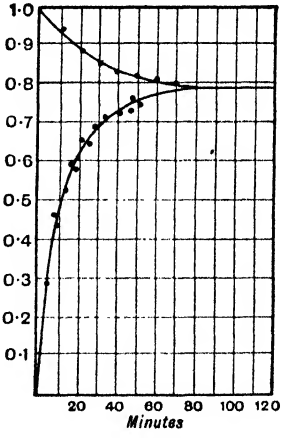


Fig. 84.—Attainment of equilibrium state.

The curves in Fig. 84 show Bodenstein's results, the abscissae being times of heating in minutes and the ordinates the fractions of HI in the mixture; the upper curve refers to the decomposition of HI and the lower to its formation from hydrogen and iodine. Both curves approach the same

equilibrium state. This behaviour is typical of all true equilibrium states. In the equilibrium state the reactions of formation and decomposition of hydrogen iodide are still going on under the same conditions and with equal velocities, so that in a given time as many molecules of hydrogen iodide are formed as are decomposed.

A true equilibrium state is always a balance of two opposite changes, and hence it is a *dynamic equilibrium* and not merely a static state. This was clearly recognised by Williamson (1850), Malaguti (1857) and Pfaundler (1857).

Although hydrogen and iodine do not react measurably at room temperature this is not a true equilibrium state, since at that temperature they should react nearly completely to form hydrogen iodide. The velocity of reaction is very slow at room temperature. It is important in studying equilibria to make sure that the system is in true equilibrium, and this is often done by using a catalyst, *e.g.* platinum, which does not change the equilibrium state (p. 144). An important test is that the same state is found by starting with either the initial or final products of a reaction (*e.g.* H_2 and I_2 *or* HI).

The simplest statement of the *condition for equilibrium* is that *the rate at which each system is formed must be equal to the rate at which it is decomposed*; its quantity then remains unchanged, and *equilibrium is a state which is independent of time.*

Homogeneous and heterogeneous equilibria.—Equilibrium states are divided into: (i) **homogeneous equilibria,** when *the system forms only one phase,* usually a gas or a liquid (sometimes solids exist in equilibrium states, *e.g.* solid solutions), and (ii) **heterogeneous equilibria,** when *the system forms more than one phase.*

Examples of homogeneous equilibria in gases are:

$$2HI \rightleftharpoons H_2 + I_2, \qquad 2NH_3 \rightleftharpoons N_2 + 3H_2,$$
$$N_2O_4 \rightleftharpoons 2NO_2, \qquad 2SO_3 \rightleftharpoons 2SO_2 + O_2,$$

and in liquids the classical example is the formation of ethyl acetate and water from acetic acid and alcohol (p. 140):

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O.$$

Examples of heterogeneous equilibria are very common. Some are mentioned on pp. 43-4, and these simple systems provide good illustrations of the idea of dynamic equilibrium from the point of view of the kinetic theory.

A liquid is in equilibrium with its vapour when as many molecules leave the liquid as return to it in a given time. A solid is in equilibrium with its saturated solution when as many molecules leave the solid per second as are caught up again. Barium peroxide in a closed vessel at constant temperature decomposes into baryta and oxygen: $2BaO_2 = 2BaO + O_2$. The oxygen molecules by collision with the baryta form barium peroxide again. At higher oxygen pressures there are more of such collisions and a greater rate of combination. The rate at which peroxide molecules break up is constant at a given temperature, hence at a certain pressure of oxygen the rate at which peroxide is formed becomes equal to the rate at which it is decomposed, and a state of equilibrium is set up: $2BaO_2 \rightleftharpoons 2BaO + O_2$. If the oxygen pressure is

raised, the collisions become more frequent and more combination takes place, and if the pressure is *maintained* above the equilibrium pressure, all the oxygen is reabsorbed by the baryta. If the pressure of the oxygen is decreased more peroxide decomposes, since less oxygen returns to it by collisions, and if gas is *continuously* pumped off all the peroxide is ultimately decomposed.

In all these examples both experiment and the Phase Rule show that *the equilibrium is independent of the amounts of the phases.*

E.g. with the reaction $2BaO_2 \rightleftharpoons 2BaO + O_2$ we have C = 2, P = 3 ;

$$\therefore \quad F = 2 + 2 - 3 = 1,$$

so that the oxygen pressure depends only on the temperature. Similarly with the dissociation of calcium carbonate : $CaCO_3 \rightleftharpoons CaO + CO_2$, or of a salt hydrate :

$$CuSO_4, 5H_2O \rightleftharpoons CuSO_4, 3H_2O + 2H_2O \text{ (vap.)}.$$

There is a difficulty here from the point of view of the kinetic theory. If we have much calcium oxide and little calcium carbonate we should expect a lower pressure of carbon dioxide than with little calcium oxide and much carbonate, because there is a larger surface with which the impinging carbon dioxide molecules can combine by collisions. This was explained by Ostwald, who pointed out that *equilibrium is set up in the surface of separation of the solids.* The carbon dioxide is at first absorbed to form a layer of calcium carbonate, and calcium carbonate on decomposing forms a layer of calcium oxide. The solids just below the surface come into equilibrium with it by loss or gain of carbon dioxide molecules, and equilibrium between the surface and the gas is attained when as many molecules enter as leave the interface.

Effect of volatility or insolubility.—A reaction often seems to go to completion instead of to a state of equilibrium. Berthollet showed that this is often due to a *disturbance of the equilibrium state* because one or more of the products, owing to their *volatility* or *insolubility*, pass into the gaseous state or deposit as solids, and cease to influence the reaction to any extent. Equilibrium states are best investigated with all the substances forming a gaseous phase or all in solution.

When concentrated sulphuric acid is poured on sodium chloride a state of equilibrium is set up momentarily : $NaCl + H_2SO_4 \rightleftharpoons NaHSO_4 + HCl$, but the hydrogen chloride escapes as gas, the equilibrium is disturbed and the reaction proceeds. When sulphuric acid is added to barium chloride solution the equilibrium $BaCl_2 + H_2SO_4 \rightleftharpoons BaSO_4 + 2HCl$ is disturbed by the precipitation of barium sulphate and the reaction seems to go to completion.

Investigation of equilibrium states.—In examining an equilibrium state it must be arranged so that reaction does not occur when the conditions are changed. One way of doing this is to heat the system until equilibrium is reached, *e.g.* $2HI \rightleftharpoons H_2 + I_2$, and then *cool it rapidly* : the reaction velocity may then become very small and the proportions of the substances, *e.g.* HI, H_2 and I_2, are practically those in the equilibrium state at the higher temperature. In some cases the cooling must be very rapid, otherwise some reaction occurs.

Grove (1847) heated a platinum wire electrically in steam. In contact with the hot wire dissociation occurs : $2H_2O \rightleftharpoons 2H_2 + O_2$, and the products pass into the surrounding steam, which cools them. Since the products of dissociation and the unchanged steam continually come in contact with the hot wire a state of equilibrium corresponding with the temperature of the wire is slowly reached.

Deville (1864) proved that some gases (H_2O, CO_2, HCl, etc.) dissociate at high temperatures by means of the apparatus shown in Fig. 85. A wide tube of

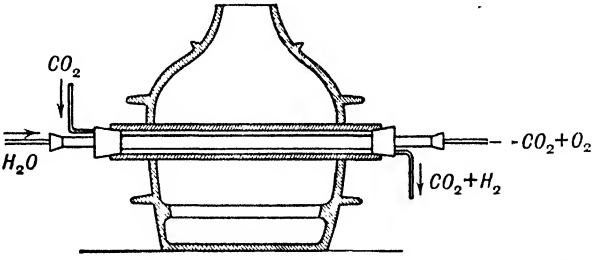


FIG. 85.—Deville's experiment. The " hot and cold " tube.

glazed porcelain, with a narrower axial tube of unglazed porcelain was strongly heated in a furnace. Water vapour was passed through the inner tube and carbon dioxide through the annular space, and the gases from both collected over alkali, which absorbed the carbon dioxide. The steam dissociated and hydrogen passed by diffusion through the porous tube, leaving much of the oxygen in the inner tube. 1 c.c. of detonating gas ($2H_2 + O_2$) was collected for every g. of water passed through the apparatus. When carbon dioxide was passed rapidly through a glazed porcelain tube packed with fragments of porcelain and heated to 1200°–1300°, dissociation occurred : $2CO_2 \rightleftharpoons 2CO + O_2$, and when the gas was collected over alkali a small volume of a mixture of carbon monoxide and oxygen was obtained.

In some cases the composition of the gaseous or liquid equilibrium system can be found by *physical methods* which do not disturb the equilibrium state, *e.g.* measurements of vapour density, electrical conductivity, volumes of liquid systems, heat changes, optical activity, light absorption, magnetism, etc. A simple case is when a product of reaction is coloured. This may be illustrated by an experiment due to J. H. Gladstone (1855 ; *J.C.S.*, 1857, **9**, 54). Ferric nitrate and ammonium thiocyanate in solution produce ferric thiocyanate which is red (see p. 864). The reaction is reversible :

$$Fe(NO_3)_3 + 3NH_4CNS \rightleftharpoons Fe(CNS)_3 + 3NH_4NO_3,$$

and if excess of $Fe(NO_3)_3$ or NH_4CNS is added the intensity of colour deepens, but if NH_4NO_3 is added, the reverse reaction is favoured and the colour becomes paler. From the colour of the solution the amount of ferric thiocyanate present may be determined and the effect of excess of the other substances calculated.

EXPT. 1.—Prepare two solutions containing 3·5 g. of crystallised ferric nitrate ($Fe(NO_3)_3,6H_2O$), and 2·3 g. of NH_4CNS per litre. Mix 100 c.c. of each. A dark red solution of $Fe(CNS)_3$ is formed. Add 25 c.c. of this to 1 litre of water in each

of four glass cylinders ; a pale brownish-red colour is produced. Keep one jar for reference and to the other three add : (*a*) 25 c.c. of the ferric nitrate solution, (*b*) 25 c.c. of the thiocyanate solution, (*c*) 25 c.c. of a saturated solution of NH_4NO_3. Observe the colour changes.

The Law of Mass Action

Many experiments (*e.g.* Gladstone's) show that an excess of a reacting substance may cause a reaction to proceed further, whilst an excess of a product of reaction drives the reaction back. This is one of many examples of the **action of mass.** Although this effect was pointed out by Berthollet (p. 124), the quantitative *law of mass action* was first deduced by Guldberg and Waage * in 1867. They replaced the rather vague idea of " chemical mass " by *concentration*, this being *the number of g. mols.* (*mols*) *per litre*, either for a gas or a solution. The concentration of a substance A is denoted by c_A or by the chemical symbol in square brackets [A].

For gaseous reactions the law of mass action may be deduced from the kinetic theory.

The deduction depends on the assumption that reaction occurs only as a result of *molecular collisions* between at least (and usually) two molecules. This is assumed even when only one kind of molecule is changing, *e.g.* when hydrogen iodide decomposes, two molecules of it enter into collision : $2HI = H_2 + I_2$. Even in cases which are apparently unimolecular : A→, the actual mechanism probably begins with a bimolecular collision : A + A→, and at very low pressures, where there are no disturbing influences, the measured reaction rate becomes of the second order (bimolecular).

Let a mixture of hydrogen and iodine vapour be heated at a constant temperature. Molecules of hydrogen iodide are formed by collisions of hydrogen and iodine molecules, the number of collisions per sec. being proportional to the number of molecules of *each* gas in unit volume, *i.e.* to its concentration. The number of collisions per sec. is thus proportional to the *product* of the concentrations. A definite fraction of the total number of collisions is supposed to result in chemical change, hence the *rate of formation* of HI is equal to $k_1 c_{H_2} c_{I_2}$, where k_1 is a constant.

At the same time hydrogen iodide molecules are decomposing by bimolecular collisions, and since *two* molecules of HI must collide the probability for this is proportional to c^2_{HI}, and hence the *rate of decomposition* of HI is equal to $k_2 c^2_{HI}$, where k_2 is a constant. Both k_1 and k_2 depend on the temperature.

The *net rate of formation* of HI is thus :

$$k_1 c_{H_2} c_{I_2} - k_2 c^2_{HI}.$$

In equilibrium the HI is decomposed just as fast as it is formed, and if c_{H_2}, etc., are now the concentrations at equilibrium :

$$k_1 c_{H_2} c_{I_2} - k_2 c^2_{HI} = 0 ;$$

$$\therefore \; c^2_{HI} / c_{H_2} c_{I_2} = k_1/k_2 = \text{const.} = K,$$

* Pronounced Vōga.

where K is called the *equilibrium constant*. It is independent of the actual amounts of iodine, hydrogen and hydrogen iodide present, but depends on the temperature; k_1 and k_2 are called the *velocity coefficients* of the reactions, and the equilibrium constant is always equal to the ratio of the velocity coefficients. This ratio is, by convention, taken so that the concentrations of the *products* of the reaction considered appear in the *numerator* and those of the reacting substances in the denominator, *e.g.* the above value of K refers to the reaction: $H_2 + I_2 = 2HI$.

A general form of the law of mass action may now be stated. Let a *reversible* chemical reaction between a molecules of a substance A, b molecules of a substance B, etc., produce l molecules of a substance L, m molecules of a substance M, etc., then the equilibrium constant of the reaction:

$$aA + bB + \ldots \rightleftharpoons lL + mM + \ldots$$

is

$$c_L^l c_M^m \ldots / c_A^a c_B^b \ldots = K, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

where c represents a concentration at equilibrium.

Although this can be deduced kinetically in the same way as in the case $H_2 + I_2 \rightleftharpoons 2HI$, collisions of more than two molecules are very rare, and apparently more complicated reactions occur in simpler stages. In such cases the *simple* kinetic deduction of the law of mass action is unsuitable, but the law can be deduced from thermodynamics, or can be regarded as established by experiment.

The law of mass action is a *quantitative law* applying to gases and (with some restrictions to be discussed later) to dilute solutions, although it is often used qualitatively to predict the effects of excess of one or more reacting substances. An example of the quantitative application of the law follows (for further examples see Partington and Stratton, *Intermediate Chemical Calculations*, Chap. X).

EXAMPLE 1.—7·94 c.c. of hydrogen (at S.T.P.) and 0·0601 g. of solid iodine were heated in a sealed bulb at 444° until equilibrium was reached. 9·52 c.c. of hydrogen iodide (at S.T.P.) were formed. Now at S.T.P. 2×127 g. of iodine (I_2) occupy 22,420 c.c. ∴ vol. of I_2 vapour at S.T.P. initially present

$$= \frac{22420 \times 0{\cdot}0601}{2 \times 127} = 5{\cdot}30 \text{ c.c.}$$

The 9·52 c.c. of HI are formed from 4·76 c.c. of H_2 and 4·76 c.c. of I_2, ∴ in equilibrium:

vol. of $H_2 = 7{\cdot}94 - 4{\cdot}76 = 3{\cdot}18$ c.c.
vol. of $I_2 = 5{\cdot}30 - 4{\cdot}76 = 0{\cdot}54$ c.c.
vol. of $HI = 9{\cdot}52$.

One mol of a gas at S.T.P. occupies 22,420 c.c. Hence, if V is the volume of the bulb in litres, the *concentrations* are:

$[H_2] = 3{\cdot}18/22420V$; $[I]_2 = 0{\cdot}54/22420V$; $[HI] = 9{\cdot}52/22420V$.

Hence:

$$K = \frac{[H_2] \times [I_2]}{[HI]^2} = \frac{3{\cdot}18 \times 0{\cdot}54}{(9{\cdot}52)^2} = 0{\cdot}01895.$$

Now, suppose 8·10 c.c. of hydrogen and 2·94 c.c. of iodine vapour (at S.T.P.) heated at 444°. What volume of HI will be formed in equilibrium? Let $2x$ c.c. be formed :

$$\begin{array}{lccccc} & H_2 & + & I_2 & \rightleftharpoons & 2HI \\ \text{Volumes :} & (8{\cdot}10 - x) & & (2{\cdot}94 - x) & & 2x \end{array}$$

$$\therefore \frac{(8{\cdot}10 - x)(2{\cdot}94 - x)}{4x^2} = 0{\cdot}01895 ;$$

$\therefore x = 2{\cdot}825$ or $9{\cdot}12$. Only the root $2{\cdot}83$ is admissible, since 2·94 c.c. of I_2 vapour can give only 5·88 c.c. of HI as a maximum. Thus, the volume of HI formed $= 2 \times 2{\cdot}83$ c.c. $= 5{\cdot}66$ c.c. Bodenstein by experiment found 5·66 c.c.

Effect of Pressure and Temperature on Equilibrium States

Effect of pressure on the equilibrium state.—Let 2 g. mols. of gaseous hydrogen iodide be heated in a volume V and let the degree of dissociation (p. 20) be α. The numbers of g. mols. in equilibrium are :

$$\begin{array}{c} 2HI \rightleftharpoons H_2 + I_2, \\ 2(1-\alpha) \quad \alpha \quad \alpha ; \end{array}$$

hence the concentrations are :

$$[HI] = 2(1-\alpha)/V, \quad [H_2] = \alpha/V, \quad [I_2] = \alpha/V ;$$
$$\therefore K = [H_2]\,[I_2]/[HI]^2 = \alpha^2/4(1-\alpha)^2,$$

which is independent of the volume V, and therefore of the pressure. *In all cases where the total volume is unchanged by a reaction, pressure has no influence on the equilibrium state.* It must be carefully noted that pressure has no effect on the equilibrium *constant* in *any* case, since this can depend only on the temperature and is independent of pressure.

If an increase of volume occurs, *e.g.* with phosphorus pentachloride :

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2.$$

$$[PCl_5] = (1-\alpha)/V, \quad [PCl_3] = \alpha/V, \quad [Cl_2] = \alpha/V,$$

$$\therefore \frac{[PCl_3]\,[Cl_2]}{[PCl_5]} = \frac{\alpha^2}{(1-\alpha)V} = K. \qquad \ldots\ldots(3)$$

The extent of dissociation α now depends on the volume V, and therefore on the pressure.

If V is increased (*i.e.* the pressure decreased), the denominator in (3) becomes larger ; the numerator and therefore α must also increase to maintain the constant value of K. Hence the dissociation increases when the pressure is reduced. The same effect is produced by adding an indifferent gas, which reduces the partial pressures.

An equation exactly like (3) is found for the dissociation of nitrogen peroxide :

$$\begin{array}{c} N_2O_4 \rightleftharpoons 2NO_2, \\ 1-\alpha \quad 2\alpha, \end{array}$$

but in this case if the *total* concentration of NO_2 is taken a factor 4 appears in the numerator:

$$4\alpha^2/(1-\alpha)V = K.$$

Instead of concentrations the *partial pressures* of gases may be used. The ratio of the partial pressure of a gas in a mixture to the total pressure is equal to the ratio of the number of molecules of that gas to the total number of molecules, since the pressures are proportional to the numbers of molecules in a given volume. In a partly dissociated mixture from 1 mol of N_2O_4 we have $(1-\alpha)$ mols of N_2O_4 and 2α mols of NO_2, or $(1+\alpha)$ mols in all. Hence if P is the total pressure:

$$p_{NO_2} = \frac{2\alpha}{1+\alpha}P, \text{ and } p_{N_2O_4} = \frac{1-\alpha}{1+\alpha}P;$$

$$\therefore \frac{p^2_{NO_2}}{p_{N_2O_4}} = \frac{4\alpha^2 P}{(1-\alpha)(1+\alpha)} = K',$$

where K' is the equilibrium constant in terms of partial pressures. This, like K, depends only on temperature and is independent of the total pressure, hence when P is increased α, the degree of dissociation, must decrease.

The *effect of pressure on equilibrium* is seen to be covered by the law of mass action. It is expressed qualitatively by **Robin's law** (1879): *increase of pressure on a system in equilibrium favours that change which occurs with decrease of volume, and decrease of pressure favours that change which occurs with increase of volume.* In the three cases:

$$2NO_2 \rightleftharpoons N_2O_4, \quad PCl_3 + Cl_2 \rightleftharpoons PCl_5, \quad N_2 + 3H_2 \rightleftharpoons 2NH_3,$$

increase of pressure causes the reaction to occur from left to right. Pressure has no influence on the reaction $2HI \rightleftharpoons H_2 + I_2$.

Robin's law is a special case of **Le Chatelier's** * **principle** (1888): *if a system in equilibrium is subjected to a constraint, a change occurs if possible of such a kind that the constraint is partially annulled.*

EXAMPLE 2.—2·0 g. of PCl_5 sealed in an evacuated bulb of 200 c.c. capacity are heated at 200°. Find the pressure developed if PCl_5 is 48·5 p.c. dissociated under 1 atm. pressure at 200° C.

2·0 g. of $PCl_5 = 2{\cdot}0/208 = 0{\cdot}0096$ g. mol. Let α = degree of dissociation under the conditions of experiment. Let the volumes be measured in litres; then

$$[PCl_5] = \frac{0{\cdot}0096(1-\alpha)}{0{\cdot}2}; \quad [PCl_3] = [Cl_2] = \frac{0{\cdot}0096\alpha}{0{\cdot}2}; \quad \therefore K = \frac{0{\cdot}0096\alpha^2}{0{\cdot}2(1-\alpha)} \quad \ldots(i)$$

At 200° under 1 atm. pressure PCl_5 is 48·5 p.c. dissociated. The volume of 1 g. mol. under these conditions is

$$22{\cdot}4 \times 1{\cdot}485 \times \frac{473}{273} = 57{\cdot}6 \text{ litres.}$$

Hence
$$K = \frac{(0{\cdot}485)^2}{0{\cdot}515 \times 57{\cdot}6} = 0{\cdot}00793. \quad \ldots(ii)$$

By equating (i) and (ii) and solving the quadratic equation we find $\alpha = 0{\cdot}332$.

* Pronounced Chăt-ĕliér, not Cha-téliĕr.

There are $1{\cdot}332 \times 0{\cdot}0096$ g. mols. in 200 c.c. or 0·2 lit., hence the pressure is

$$1{\cdot}332 \times 0{\cdot}0096 \times (22{\cdot}4/0{\cdot}2) \times (473/273) = 2{\cdot}48 \text{ atm.}$$

The degree of dissociation falls from 0·485 to 0·332 when the pressure is raised from 1 to 2·48 atm.

Effect of products of dissociation.—The law of mass action shows at once the effect of adding an excess of one product of dissociation at *constant volume*.

In the case of hydrogen iodide: $[H_2]\,[I_2]/[HI]^2 = K$, hence if excess of H_2 or I_2 vapour is added, the value of the product on the left can remain equal to K (at constant volume) only if [HI] increases, *i.e.* the extent of dissociation is reduced.

In the case of phosphorus pentachloride: $[PCl_3]\,[Cl_2]/[PCl_5] = K$, it is seen that increase of $[Cl_2]$ or $[PCl_3]$ must result in an increase of $[PCl_5]$, *i.e.* the dissociation is reduced.

The effect of adding a product of dissociation at *constant pressure* is less obvious.

EXAMPLE 3.—Let 2 mols of HI be heated at 444° until equilibrium is reached and let α be the degree of dissociation:

$$\begin{array}{ccccc} 2HI & \rightleftharpoons & H_2 & + & I_2, \\ 2(1-\alpha) & & \alpha & & \alpha. \end{array}$$

Then $\alpha^2/4(1-\alpha)^2 = K = 0{\cdot}01895$ (see Example 1);

$$\therefore\ \alpha/(1-\alpha) = \pm\sqrt{0{\cdot}0758} = \pm 0{\cdot}2754; \quad \therefore\ \alpha = 0{\cdot}216.$$

Let a further 1 mol of H_2 be added at *constant pressure* and let the degree of dissociation change to α'. Then

$$\begin{array}{ccccc} 2HI & \rightleftharpoons & H_2 & + & I_2, \\ 2(1-\alpha') & & \alpha'+1 & & \alpha'; \end{array}$$

$$\therefore\ \alpha'(1+\alpha')/4(1-\alpha')^2 = K = 0{\cdot}01895.$$

$\therefore\ \alpha' = 0{\cdot}063$. Hence the dissociation is reduced.

EXAMPLE 4.—Let 1 mol of PCl_5 be heated at 200° at 1 atm. pressure and let a further 2 mols of PCl_3 vapour be added at *constant pressure*. If α' is the degree of dissociation (previously 0·485, Ex. 2) and V' the total volume:

$$\begin{array}{ccccc} PCl_5 & \rightleftharpoons & PCl_3 & + & Cl_2, \\ 1-\alpha' & & 2+\alpha' & & \alpha'. \end{array}$$

$$[PCl_5] = (1-\alpha')/V'; \quad [PCl_3] = (2+\alpha')/V', \quad [Cl_2] = \alpha'/V';$$

$$\therefore\ \alpha'(2+\alpha')/(1-\alpha')V' = K = 0{\cdot}00793. \qquad \text{.....(i)}$$

The total no. of mols is $(1-\alpha') + (2+\alpha') + \alpha' = 3+\alpha'$.

$$\therefore\ V' = 22{\cdot}4 \times (3+\alpha') \times \frac{T}{273} \times \frac{760}{p} \text{ lit.} \qquad \text{.....(ii)}$$

With $p = 760$ mm. and $T = 473$ we find from (i) and (ii):

$$\alpha'(2+\alpha')/(3+\alpha')(1-\alpha') = 0{\cdot}3079. \quad \therefore\ \alpha' = 0{\cdot}306.$$

Hence the dissociation is reduced.

Wurtz (1873) volatilised PCl_5 in a Dumas vapour density bulb filled with chlorine or PCl_3 vapour and determined the weight of gas after sealing. He then analysed the content of the bulb and calculated that the vapour density corresponded with undissociated PCl_5.

Heterogeneous reactions.—When pure solids are present in a system their vapour pressures or solubilities are constant at a given temperature and in the expression for the law of mass action for a gaseous or homogeneous solution phase in a heterogeneous system the constant concentrations referring to the pure solids may be included in the equilibrium constant.

As an example, consider the action of steam on red-hot iron

$$3Fe + 4H_2O \rightleftharpoons Fe_3O_4 + 4H_2.$$

In the gaseous phase, to which alone the law of mass action applies, we may assume that in addition to H_2O and H_2 at measurable and variable pressures, the vapours of the iron and oxide of iron are present also at immeasurably small and constant pressures. In

$$K = \frac{[Fe_3O_4]\,[H_2]^4}{[Fe]^3\,[H_2O]^4},$$

since $[Fe_3O_4]$ and $[Fe]$ are constant, we can write :

$$K = \frac{[Fe_3O_4]}{[Fe]^3} \cdot \frac{[H_2]^4}{[H_2O]^4} = k \cdot \frac{[H_2]^4}{[H_2O]^4},$$

or

$$K_1 = [H_2]/[H_2O],$$

where

$$K_1 = \sqrt[4]{K/k}.$$

Hence the ratio of the concentrations or partial pressures of the hydrogen and steam is constant at a given temperature and independent of the amounts of iron and iron oxide. This result is often expressed by saying that " the active masses of pure solids are constant," but the meaning of this should be carefully noted.

In the isochore equation (4) the equilibrium constant K contains only the concentrations of the gases, but q_v is the heat change for the total reaction.

Effect of temperature on equilibrium.—The effect of temperature on an equilibrium state cannot be deduced from the law of mass action, since in this case the equilibrium constant changes. Qualitatively the effect is expressed by van't Hoff's **law of mobile equilibrium** (1884), which is a special case of Le Chatelier's principle (p. 132) : *when the temperature of a system in equilibrium is raised that change occurs which absorbs heat, and when the temperature is lowered that change occurs which evolves heat.* In other words, *rise in temperature induces an endothermic change and fall in temperature an exothermic change.*

In three typical cases :

$2HI \rightleftharpoons H_2 + I_2$	$K = [H_2]\,[I_2]/[HI]^2$
$PCl_5 \rightleftharpoons PCl_3 + Cl_2$	$K = [PCl_3]\,[Cl_2]/[PCl_5]$
$N_2O_4 \rightleftharpoons 2NO_2$	$K = [NO_2]^2/[N_2O_4]$

there is absorption of heat in the reaction from left to right, hence rise in temperature increases the dissociation in each case. In the reactions

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 \qquad K = [NH_3]^2/[N_2]\,[H_2]^3$$
$$2SO_2 + O_2 \rightleftharpoons 2SO_3 \qquad K = [SO_3]^2/[SO_2]^2[O_2]$$

there is evolution of heat, hence rise in temperature decreases the quantities of NH_3 and SO_3 in equilibrium.

The effect of temperature on the equilibrium constant may be calculated by thermodynamics for reactions in gases or dilute solutions.

If T is the absolute temperature, q_v the heat of reaction at constant volume *absorbed* in g. cal., and **R** the gas constant (2 g. cal./1°) :

$$\ln K = -q_v/\mathbf{R}T + \text{const.}, \qquad \ldots\ldots(4)$$

where ln is the natural logarithm to the base e, and with two temperatures and with common logarithms :

$$\log \frac{K_2}{K_1} = \frac{q_v}{4{\cdot}57}\left(\frac{1}{T_1} - \frac{1}{T_2}\right). \qquad \ldots\ldots(5)$$

This is van't Hoff's *reaction isochore equation*. By plotting log K against $1/T$ a straight line is obtained, from the slope of which q_v may be calculated.

For endothermic reactions q_v is positive, and (4) shows that K increases with rise in temperature ; for exothermic reactions q_v is negative, and K decreases with rise in temperature. This agrees with the qualitative results.

The effect of temperature on *equilibrium* must be carefully distinguished from its effect on *reaction velocity* (p. 141). The velocities of practically *all* reactions increase rapidly with temperature. At lower temperatures some reactions are so slow that they cannot be detected, even in presence of catalysts. At higher temperatures the reaction velocity becomes appreciable, but the equilibrium yield may be smaller than at lower temperatures. In practice a good catalyst is used and the temperature kept as low as it can be, yet high enough to give a suitable velocity. The requirements of yield and velocity are conflicting, and the best compromise must be adopted.

Velocity of Reaction

The study of equilibrium states is called *chemical statics*, and it goes back to C. L. Berthollet (1799). The study of the velocities or rates of chemical reactions is called *chemical dynamics* ; it opened with some experiments of C. F. Wenzel (1777) on the rates of solution in acids of small cylinders of metals waxed except at one end, which showed that " if an acid dissolves one part of copper in an hour, an acid half as strong will take two hours to dissolve the same amount of copper, the surface exposed and temperature remaining the same." This is the first recognition of the *action of mass*. Since reaction velocities in such heterogeneous systems are complicated by diffusion, etc., it is better to work in homogeneous systems, and the first experiments on this case were made by L. Wilhelmy (1850), who studied the rate of conversion of cane sugar into invert sugar in a solution containing an acid.

The *velocity* of a chemical change is measured by *the quantity of substance in unit volume changed in unit time.* The quantity is measured in g. mols., and since the velocity changes as the substance is used up it is necessary to consider the small change δx g. mols. in a very small time interval δt, the velocity being the limiting value of $\delta x/\delta t$ when δt approaches zero, *i.e.* dx/dt. If c is the concentration of the substance changing, in g. mols. in unit volume, then clearly $\delta x = -\delta c$, and hence $dx/dt = -dc/dt$, the concentration getting less as the amount of change increases.

Unit volume is usually 1 litre, unit time may be a second, minute, hour or day according to the velocity of the reaction.

The *law of mass action* states that *the velocity with which any substance changes is proportional to its concentration, and if several substances take part, to the product of the concentrations* (see p. 129).

Reactions are classified according to *order* by the value of n in the velocity equation :

$$-dc/dt = kc^n, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(6)$$

where k is the velocity coefficient. According as n is 1, 2 or 3 we have *first, second* and *third order reactions.*

This so-called *kinetic order* of a reaction may not be (although it often is) the same as *molecular order,* or number of reacting molecules shown by the ordinary chemical equation for the complete reaction, when the reactions may be said to be *unimolecular, bimolecular* or *termolecular.* The order and molecularity will differ when a reaction takes place in successive stages, when the measured velocity is obviously that of the *slowest* stage, on which all the faster stages must depend. The kinetic order is not often greater than two.

In a *unimolecular reaction* $A \rightarrow$

$$-dc/dt = kc,$$

and in a *bimolecular reaction* of one substance $2A \rightarrow$

$$-dc/dt = kc^2,$$

or for two substances $A + B \rightarrow$

$$-dc/dt = kc_A c_B$$

where $-dc/dt$ is the rate of disappearance of either A or B.

These equations apply if the reaction is irreversible ; if there is a back reaction, *e.g.*

$$A + B \rightleftharpoons C + D$$

$$-dc_A/dt = -dc_B/dt = dc_C/dt = dc_D/dt = k_1 c_A c_B - k_2 c_C c_D,$$

and in equilibrium the velocity is zero ;

$$\therefore\ k_1 c_A c_B = k_2 c_C c_D\ ; \quad \therefore\ \frac{c_C c_D}{c_A c_B} = \frac{k_1}{k_2} = K,$$

where K is the equilibrium constant.

The velocity of reactions involving *ions* is affected by the presence of chemically indifferent ions, and in very dilute solutions the velocity coefficient k is given by Brönsted's equation :

$$\log k = \log k_0 + z_1 z_2 \sqrt{I},$$

where I is the *ionic strength* $\frac{1}{2}\Sigma c_i z_i^2$ (p. 167), *i.e.* half the sum of the concentrations c_i of each ion multiplied by the square of its valency z_i ; k_0 is the value of k for zero ionic strength, and z_1, z_2 are the valencies (with proper signs) of two ions undergoing reaction (see Moelwyn-Hughes, *Kinetics of Reactions in Solution*, 1933, Chap. VII).

First order reactions.—A reaction studied by Wilhelmy (1850) was the *inversion of cane sugar* $C_{12}H_{22}O_{11}$ into dextrose $C_6H_{12}O_6(d)$ and levulose $C_6H_{12}O_6(l)$ in solution in a dilute acid, which acts as a *catalyst* (p. 142) and itself undergoes no permanent change (although the hydrogen ion probably takes part in the reaction) :

$$C_{12}H_{22}O_{11} + H_2O = C_6H_{12}O_6 d + C_6H_{12}O_6 l.$$

Since cane sugar rotates the plane of polarised light to the right and the mixture of two sugars formed (" invert sugar ") rotates it to the left, the amount of change is followed by measuring the angle of rotation θ from time to time by a polarimeter.

The reaction is really bimolecular, but since the water is present in such large excess its concentration remains practically constant and the reaction is one of the first order ; it may be called a *pseudo-unimolecular reaction.* If c is the concentration of cane sugar present at any time the velocity equation is :

$$-\mathrm{d}c/\mathrm{d}t = kc. \qquad \ldots\ldots(7)$$

Integration gives $-\ln c = kt + \text{const.}$, where " ln " denotes the natural logarithm to the base e. When $t = 0$, $c = c_0$ the initial concentration, hence the constant is $-\ln c_0$.

$$\therefore \ln c_0 - \ln c = 2{\cdot}3026\,(\log c_0 - \log c) = kt,$$

where " log " is the logarithm to the base 10,

$$\therefore k = \frac{2{\cdot}3026}{t} \log \frac{c_0}{c},$$

or

$$k' = \frac{k}{2{\cdot}3026} = 0{\cdot}4343k = \frac{1}{t} \log \frac{c_0}{c}. \qquad \ldots\ldots(8)$$

Since

$$\log c = \log c_0 - 0{\cdot}4343kt,$$

the logarithm of c plotted against t gives a straight line. From the values of c and t the value of k may be calculated.

Wilhelmy found the following results :

t min. -	0	30	90	150	240	450	570	∞
θ - -	46·75	41·00	30·75	22·00	11·50	- 4·50	- 8·75	- 18·70
$\log (c_0/c)$	—	0·0399	0·1217	0·2063	0·3359	0·6636	0·8181	—
$10^3 \times k'$ -	—	1·33	1·35	1·38	1·40	1·47	1·44	—

The amount of cane sugar present at any time is proportional to the difference between the angle of rotation at that time and the angle of rotation at the end of the reaction, *i.e.* to $\theta - (-18{\cdot}70) = \theta + 18{\cdot}70$, where θ is taken with the correct sign. The amount of cane sugar present at the start is proportional to the total change of rotation $46{\cdot}75 - (-18{\cdot}70) = 65{\cdot}45$. Hence $c_0/c = 65{\cdot}45/(\theta + 18{\cdot}70)$. The values of $k' = 0{\cdot}4343k$ calculated are nearly constant (see Worley, *J.C.S.*, 1911, **99**, 349).

Another pseudo-unimolecular reaction is the *hydrolysis of methyl acetate* by dilute acid acting as a catalyst :

$$CH_3COOCH_3 + H_2O = CH_3COOH + CH_3OH.$$

EXPT. 2.—100 c.c. of $N/2$ HCl is measured into a stoppered bottle immersed in a thermostat at 25°. Some freshly distilled methyl acetate in a small flask is also immersed in the thermostat and 5 c.c. of it pipetted into the acid and the time noted. The mixture is shaken and 2 c.c. at once pipetted into 50 c.c. of carbon dioxide-free distilled water, when the reaction practically stops. The diluted mixture is titrated with $N/20$ baryta and phenolphthalein ; suppose x c.c. are required. After intervals of 10, 20, 30, 40, 60 and 120 mins. the withdrawal of 2 c.c. of reaction mixture and titration are repeated, and the baryta titre minus x gives the amount of acetic acid formed. A final titration after 48 hours gives the acetic acid for the complete reaction, *i.e.* the original amount of methyl acetate.

If x is the amount in g. mols. of methyl acetate hydrolysed after a time t and a the initial amount,

$$dx/dt = k(a - x) \; ; \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (9)$$

$\therefore$ by integration $\log a - \log (a - x) = 0{\cdot}4343kt$;

$$\therefore \; k = \{\log a - \log (a - x)\}/0{\cdot}4343t. \quad \ldots\ldots\ldots\ldots\ldots\ldots (10)$$

Ostwald (1883) found the following results (k' is $0{\cdot}4343k$) :

t min.	-	-	14	34	89	159	239	399
$\log \frac{a}{a-x}$	-	-	0·0292	0·0716	0·1858	0·3354	0·5129	0·8539
$10^3 \times k'$	-	-	2·09	2·11	2·09	2·11	2·15	2·14

Harcourt and Esson (*Phil. Trans.*, 1895, **186**, 817) studied the reaction :

$$H_2O_2 + 2HI = 2H_2O + I_2.$$

By adding known constant amounts of sodium thiosulphate as soon as iodine appeared and having excess of sulphuric acid present the hydriodic acid concentration was kept constant :

$$I_2 + 2Na_2S_2O_3 = Na_2S_4O_6 + 2NaI$$
$$2NaI + H_2SO_4 \quad = Na_2SO_4 + 2HI.$$

The reaction was found to be of the first order with respect to hydrogen peroxide, which is the only reacting substance changing in concentration.

EXPT. 3.—Dissolve a few crystals of KI in 20 c.c. of 1 : 6 H_2SO_4, dilute to 200–300 c.c. and add some starch solution to form solution A. Measure out into

each of ten test-tubes 5 c.c. of $N/10$ $Na_2S_2O_3$. To A add 20 c.c. of 0·3 p.c. H_2O_2 and as soon as a blue colour appears note the time and at once add a 5 c.c. portion of thiosulphate and shake. The blue colour disappears. When the blue colour reappears note the time, add a further 5 c.c. of thiosulphate and continue the experiment in this way. The concentrations of unchanged H_2O_2 are calculated from the amount of thiosulphate added, and on plotting the logarithms of these against the times a straight line should result, from the slope of which k can be found. Also plot $[H_2O_2]$ against time and note how the amount of H_2O_2 changed in equal intervals of time decreases.

Harcourt and Esson found the following results: a = orig. amt. of H_2O_2 = 20·95, x = amt. of H_2O_2 changed (both expressed in the same arbitrary units) and $k' = 0{\cdot}4343k$ calculated from (10).

t min. -	4·57	19·87	31·68	45·23	61·12	80·08	103·88	291·18
x - -	1	4	6	8	10	12	14	20
$\log \frac{a}{a-x}$	0·0213	0·0920	0·1465	0·2089	0·2818	0·3694	0·4792	1·3435
$10^3 \times k'$	4·66	4·63	4·62	4·62	4·61	4·62	4·61	4·61

The complete reaction: $2HI + H_2O_2 = I_2 + 2H_2O$ is found to be of kinetic order 2, whilst the molecular order is 3. It occurs in two stages:

$$HI + H_2O_2 = HOI + H_2O \text{ (slow)},$$
$$HI + HOI = I_2 + H_2O \text{ (very rapid)}.$$

and the order 2 is that of the slower stage. (In the above experiment, with [HI] constant, the order referred to H_2O_2 alone is 1.)

Another good experimental example of a pseudo-unimolecular reaction is the oxidation of iodide by persulphate in neutral solution in presence of excess of iodide (Price, 1898; see Palmer, *Experimental Physical Chemistry*, Cambridge, 1941, 245):

$$S_2O_8'' + 2I' = I_2 + 2SO_4''.$$

A first order homogeneous gas reaction is the thermal decomposition of nitrogen pentoxide (Daniels and Johnston, *J.A.C.S.*, 1921, **43**, 53), which takes place in two stages:

$$N_2O_5 = N_2O_3 + O_2,$$
$$N_2O_3 + N_2O_5 = 2N_2O_4 \text{ (rapid)}.$$

Some apparently first order gas reactions really take place on the walls of the vessel.

Second order reactions.—A classical example of a second order (bimolecular) reaction is the "saponification" of ethyl acetate by sodium hydroxide in a large amount of water, when alcohol and sodium acetate are formed (Warder, 1881):

$$CH_3COOC_2H_5 + OH' = CH_3COO' + C_2H_5OH.$$

EXPT. 4.—The procedure is similar to that of Expt. 2, but the alkali is titrated with standard acid. The solutions may be $\frac{1}{20}$ molar (0·444 g. ethyl acetate in 100 c.c.), 50 c.c. of each are mixed and 5 c.c. portions pipetted into 10 c.c. of $N/20$ HNO_3 and back-titrated with $N/40$ NaOH and phenolphthalein. Steamed-

out hard glass flasks, to prevent solution of alkali from the glass, are used, and the alkali should be free from carbonate (some baryta may be added).

For a bimolecular reaction with equal initial concentrations $a = b$ of A and B the velocity equation is :

$$dx/dt = k(a-x)(b-x) = k(a-x)^2, \quad \ldots\ldots\ldots\ldots\ldots\ldots (11)$$

integration of which gives

$$\frac{1}{a-x} - \frac{1}{a} = kt \quad \text{or} \quad \frac{1}{t} \cdot \frac{x}{a-x} = ak = \text{const.} \quad \ldots\ldots\ldots\ldots\ldots\ldots (12)$$

Warder found the following results. The alkali added required 16·00 c.c. of standard acid, A is the titration for the total reacting mixture and

$$x = 16{\cdot}00 - A \; ; \; a = 16{\cdot}00.$$

t min. -	5	15	25	35	55	120
A c.c. -	10·24	6·13	4·32	3·41	2·31	1·10
x - -	5·76	9·87	11·68	12·59	13·69	14·90
$x/(a-x)$ -	0·563	1·610	2·704	3·69	5·93	13·55
ak - -	0·113	0·107	0·108	0·105	0·108	0·113

The esterification of acetic acid, studied by Berthelot and Péan de Saint Gilles (1862–3) is a *reversible* bimolecular reaction :

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O \; ;$$
$$\therefore \; dx/dt = k_1(1-x)^2 - k_2x^2$$

when equimolecular amounts $a = b = 1$ are taken. At equilibrium the velocity is zero. $\therefore \; x^2/(1-x)^2 = k_1/k_2 = K$. It was found that two-thirds of the acid and alcohol reacted. $\therefore \; x = \frac{2}{3}$ and $K = 4$. For 2 mols of acid and 1 mol of alcohol $x^2/(1-x)(2-x) = 4$; $\therefore \; x = 0{\cdot}845$ (obs. 0·858). Although the direct and reverse velocities increase rapidly with temperature, K is nearly independent of temperature.

Very few reactions of kinetic order higher than 2 are known ; termolecular gas reactions definitely known are $2NO + X_2 = 2NOX$, where X = O, Cl or Br, and these may really be bimolecular, involving an associated molecule present in small amount, *e.g.* $(NO)_2 + O_2 = 2NO_2$. In this case $dx/dt = k[(NO)_2]\,[O_2]$. But as there is an equilibrium $2NO \rightleftharpoons (NO)_2$ we have $[(NO)_2] = K[NO]^2$;

$$\therefore \; dx/dt = kK[NO]^2[O_2],$$

and the reaction is of the third order. This mechanism is in agreement with the *decrease* of reaction velocity with rise of temperature, owing to dissociation of $(NO)_2$ molecules.

Consecutive reactions.—If a reaction takes place with formation of an *intermediate product* B which then decomposes to form C,

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

where k_1 and k_2 are the velocity coefficients, the concentration of A steadily

decreases and that of C steadily increases. The concentration of B, however, at first increases, but as its rate of change into C increases with its concentration, this reaches a maximum and then falls to zero at the end of the reaction (Fig. 86).

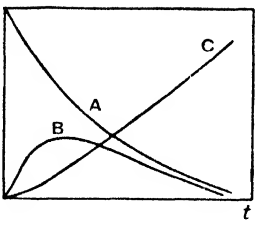


FIG. 86.—Curves of successive reactions.

In the reduction of permanganate by oxalic acid in dilute sulphuric acid in presence of some manganous sulphate as a catalyst, the pink colour changes first to brownish-red, then yellow, and finally colourless. Harcourt and Esson (*Phil. Trans.*, 1866, **156**, 193; Bradley and van Praagh, *J.C.S.*, 1938, 1624) concluded that the permanganate $Mn^{VII}O_4'$ is first reduced to a compound of 3-valent manganese Mn^{III}, which first accumulates in the solution and then disappears by reduction to a manganous salt Mn^{II}.

EFFECT OF TEMPERATURE ON REACTION VELOCITY

With very few exceptions (*e.g.* the oxidation of NO) *the velocity of a chemical reaction increases rapidly with rise of temperature*, in most cases being approximately doubled by a rise of 10°. Since the velocity increases in geometrical progression as the temperature increases in arithmetical progression, the dependence of k on temperature (absolute) is given by the equation proposed by Arrhenius in 1889:

$$\ln k = -A/T + B, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (13)$$

where A and B are constants. When $\log k$ is plotted against $1/T$ a straight line results, from the slope of which A can be calculated. Since the frequency of collisions of the molecules increases with rise of temperature it might be supposed that the increased velocity was due to this, but a calculation shows that in a gas the collision frequency increases at a rate proportional to $\sqrt{T}$, whereas the velocity increases at a much faster rate. Again, the actual velocity is much smaller than it would be if each collision were effective in causing reaction.

The number of collisions per sec. per c.c. is (p. 32)

$$2N^2d^2\sqrt{\pi \mathbf{R}T/M},$$

where N is the no. of molecules per c.c., d is the molecular diameter, M the molecular weight, and $\mathbf{R} = 8{\cdot}3 \times 10^7$ ergs per 1°.

For hydrogen iodide at 556° abs. at a concentration of 1 mol in 22·4 lit., $N = 2{\cdot}7 \times 10^{19}$ (p. 48), $d = 3{\cdot}5 \times 10^{-8}$, and hence the no. of collisions per c.c. per sec. is $6{\cdot}015 \times 10^{28}$. Each collision involves two HI molecules, hence the no. of HI molecules colliding per c.c. per sec. is $2 \times 6{\cdot}015 \times 10^{28} = 1{\cdot}2 \times 10^{29}$. Bodenstein found that $9{\cdot}42 \times 10^{-7}$ g. mols. (1 g. mol = $6{\cdot}03 \times 10^{23}$ molecules) were decomposed per minute, *i.e.*

$$9{\cdot}42 \times 10^{-7} \times (6{\cdot}03 \times 10^{23})/22400 \times 60 = 4{\cdot}3 \times 10^{11}$$

molecules per c.c. per sec. Hence only a fraction,

$$4{\cdot}3 \times 10^{11}/1{\cdot}2 \times 10^{29} = 3{\cdot}6 \times 10^{-18},$$

of the colliding molecules actually react.

Arrhenius suggested that reaction on collision occurs only between *activated molecules* having energies higher than the average value corresponding with the temperature, the molecular velocities varying according to Maxwell's distribution law (p. 28). The excess energy is in the form of vibrational energy (p. 34). The fraction of activated molecules increases rapidly with rise of temperature.

A comparison of equation (13) and equation (4) on p. 135 suggests that $A = q_a/\mathbf{R}$, q_a being a *heat of activation* corresponding with q_v, the active and inactive molecules being in equilibrium.

Hence $$\ln k = -q_a/\mathbf{R}T + B.$$

When $q_a = 0$ all the colliding molecules react.

$$\therefore\ B = \ln k_0,$$

where k_0 is the reaction velocity coefficient for this case. Hence

$$\ln k/k_0 = -q_a/\mathbf{R}T, \quad \text{or} \quad k/k_0 = e^{-q_a/\mathbf{R}T}.$$

Thus $$\frac{\text{no. of molecules decomposing per sec.}}{\text{no. of molecules colliding per sec.}} = e^{-q_a/\mathbf{R}T}.$$

For hydrogen iodide this is $3{\cdot}6 \times 10^{-18}$, $T = 556$, $\mathbf{R} = 2$ g. cal. per 1°.

$$\therefore\ q_a = -2 \times 556 \times 2{\cdot}3026 \log (3{\cdot}6 \times 10^{-18}) = 44{,}700 \text{ g. cal.}$$

This is a large quantity. It is clear that reactions with *lower* heats of activation are faster than those with larger at a given temperature.

By plotting log k against $1/T$ for several temperatures a value of $q_a = 43{,}900$ g. cal. may be calculated from the slope of the line, and this agrees satisfactorily with that calculated above (see Hinshelwood, *Kinetics of Chemical Change in Gaseous Systems*, 1940).

Catalysis

Although the word *catalysis* is used in the first text-book of chemistry, the *Alchymia* of Libavius (1597), and Evelyn in his *Diary* laments "the sad catalysis of our times," it was Berzelius in 1835 who first applied it to describe a group of chemical reactions which has been greatly enlarged since his time. *A* **catalyst** *is a substance which alters the rate of a chemical reaction without itself undergoing a permanent chemical change* (see p. 144). *Catalytic reactions* may be (i) *homogeneous*, when they occur in one phase, or (ii) *heterogeneous*, when more than one phase is present.

The action of acid in the hydrolysis of cane sugar or methyl acetate is an example of homogeneous catalysis; the action of manganese dioxide in the decomposition of potassium chlorate, and of platinum in the formation of sulphur trioxide from sulphur dioxide and oxygen, are examples of heterogeneous catalysis.

Berzelius explained catalysis as due to a peculiar "catalytic force." Since a catalyst always has the same chemical composition after the reaction (although its *physical* state may change) it seems to act by its mere presence, and catalysis

was called *contact action* by Mitscherlich in 1834. Very small quantities of a catalyst may cause the chemical change of large amounts of materials, although in some cases the catalyst in the end may become inactive, as in the case of enzymes.

Negative catalysts slow down reactions, *e.g.* the decomposition of hydrogen peroxide is retarded by an acid. Sometimes a catalyst may be deactivated by a *catalyst poison*, as colloidal platinum by cyanides or mercury salts in the decomposition of hydrogen peroxide, and the platinum by arsenic compounds in the formation of sulphur trioxide.

Ostwald supposed that a catalyst can accelerate only a reaction which is itself taking place very slowly, but then the uncatalysed reaction must sometimes be almost infinitely slow, and there seems no reason why a catalyst should not actually start a reaction. In some cases different catalysts favour different reactions, so that *the action of a catalyst may be specific.*

Carbon monoxide and hydrogen in presence of a nickel catalyst at 380° at atmospheric pressure form methane and carbon dioxide :

$$2CO + 2H_2 = CH_4 + CO_2,$$

but at 300° under 300 atm. pressure in presence of a catalyst composed of zinc oxide with 10 p.c. of chromic oxide (Cr_2O_3) methyl alcohol is formed :

$$CO + 2H_2 = CH_3OH.$$

Sometimes (as with the chromic oxide in the above example) *a substance increases the activity of the main catalyst*, and it is then called a *promoter.*

In many cases the *physical form* of the catalyst is important ; in the formation of sulphur trioxide from sulphur dioxide and oxygen, finely divided platinum (such as platinised asbestos) is used, but in the oxidation of ammonia to nitric oxide :

$$4NH_3 + 5O_2 = 4NO + 6H_2O,$$

platinum wire in the form of nets is used, since platinised asbestos is too active and causes loss by promoting the reaction :

$$4NH_3 + 3O_2 = 2N_2 + 6H_2O.$$

Among the **general properties of catalysts** may be mentioned :

(i) *A very small quantity of catalyst may be sufficient.*

Titoff (1903) found that 1 g. atom of copper ion in 10^{18} c.c. had a perceptible action in promoting the oxidation of sulphur dioxide or sulphites in solution. In some cases the trace of alkali dissolved from a glass vessel by water may exert a marked catalytic action.

(ii) *The increase in reaction velocity may be proportional to the quantity of catalyst present.*

The rate of hydrolysis of methyl acetate may be used to determine the concentration of hydrogen ion acting as a catalyst (p. 138).

(iii) *The catalyst does not undergo any permanent chemical change.* It must be carefully noted, however, that *it may take part in the reaction*, but it must then be re-formed at the end, possibly in a different physical state, *e.g.* the platinum wire in the oxidation of ammonia becomes roughened, and manganese dioxide in the decomposition of potassium chlorate more finely divided.

(iv) *A catalyst in reversible reactions has no influence on the final equilibrium state*, and hence *the velocities of the forward and reverse reactions must be equally influenced by the catalyst, i.e. the velocity coefficients k_1 and k_2 must be altered in the same ratio.*

Platinum, at the same temperature, accelerates both the combination of hydrogen and iodine and the decomposition of hydrogen iodide, and the final equilibrium state is the same with and without the catalyst, although it is reached more rapidly with the catalyst: $H_2 + I_2 \rightleftharpoons 2HI$. This was proved experimentally by Lemoine (1877) and Bodenstein (1894). It should be remembered that many catalysed reactions are non-reversible, *e.g.* the decomposition of potassium chlorate by heat in presence of manganese dioxide.

Theories of catalysis.—Many explanations of catalysis have been given and it is not likely that one will cover all the cases. A theory which seems to apply in a large number of cases is the *intermediate compound* theory, proposed by Clement and Desormes in 1806 to explain the catalytic action of oxides of nitrogen in the lead chamber process. In this sulphur dioxide, oxygen and water are converted into sulphuric acid in presence of nitrous gases:

$$(a) \quad 2SO_2 + O_2 + 2H_2O = 2H_2SO_4.$$

Nitrogen dioxide may react with sulphur dioxide and water to form sulphuric acid and nitric oxide:

$$(b) \quad SO_2 + NO_2 + H_2O = H_2SO_4 + NO,$$

and the nitric oxide is then oxidised by atmospheric oxygen to nitrogen dioxide, which again enters into reaction:

$$(c) \quad NO + \tfrac{1}{2}O_2 = NO_2.$$

The sum of reactions (*b*) and (*c*) multiplied by 2 gives (*a*). In this case the catalyst is NO, which undergoes a *cycle of reactions*, being constantly regenerated. It is necessary, of course, that the velocity of the reactions (*b*) and (*c*) involving the *intermediate compound* NO_2 shall be greater than the velocity of the direct reaction (*a*) without the catalyst. Other intermediate compounds, *e.g.* nitroso-sulphuric acid or "chamber crystals," $SO_2(OH)\cdot O\cdot NO$, have been proposed instead of NO_2, and in many cases there are such alternatives.

Hydrogen peroxide evolves oxygen with acidified iodate solution, and there is an alternation of decolorisation and reappearance of colour (Bray, *J.A.C.S.*, 1921, **43**, 1262; Abel, *Z. phys. Chem.*, 1920, **96**, 1):

$$H_2O_2 + I_2 = O_2 + 2HI, \qquad H_2O_2 + 2HI = I_2 + 2H_2O,$$

or $$5H_2O_2 + I_2 = 2HIO_3 + 4H_2O, \qquad 5H_2O_2 + 2HIO_3 = I_2 + 5O_2 + 6H_2O.$$

The catalytic action of moisture in the combustion of carbon monoxide (p. 482) was explained by Dixon (1880) as due to the cycle of changes :

$$CO + H_2O = CO_2 + H_2$$
$$H_2 + \tfrac{1}{2}O_2 = H_2O.$$

Even in such cases as the inversion of cane sugar by acids (p. 137) it is now thought probable that the hydrogen ion first combines with the reacting substance.

Mercer (1842) and Playfair (*Mem. C.S.*, 1847, **3**, 348) suggested that " almost all cases of catalytic action may be reduced to feeble chemical affinity " ; the catalyst " acts by adding its affinity to that of another body, or by exerting an attraction sufficient to effect decomposition under new circumstances." The " assisting affinity " of the catalyst must be weak, so that a compound formed by it can be decomposed again to form the original catalyst.

This is illustrated by the catalytic action of cuprous chloride CuCl in the Deacon reaction (p. 771), the weak affinity of the CuCl for chlorine adding to the strong affinity of oxygen for hydrogen in bringing about the decomposition of hydrogen chloride :

$$2H_2O \leftarrow O_2 \left\{ \begin{matrix} H \,|\, Cl \\ H \,|\, Cl \\ H \,|\, Cl \\ H \,|\, Cl \end{matrix} \right\} 4CuCl \rightarrow 4CuCl_2.$$

The cupric chloride then decomposes into chlorine and the original catalyst, cuprous chloride : $4CuCl_2 = 4CuCl + 2Cl_2$, and the reaction begins again.

Heterogeneous catalysis.—H. Davy in 1816 found that a heated platinum or palladium wire glows in a mixture of air with methane, alcohol vapour, etc., and the substances are oxidised. Other metals such as iron or copper have little action. Similar *contact actions* were investigated by Dulong and Thenard, and Döbereiner in 1823 constructed a lamp (Fig. 87) in which a jet of hydrogen generated in the apparatus from a piece of zinc and dilute acid was actually kindled by impinging on platinum sponge, or on a bundle of fine platinum wires. Faraday in 1833 found that a mixture of hydrogen and oxygen combines, sometimes with explosion, in contact with clean platinum foil ; that platinum does not catalyse the combination of hydrogen and chlorine ; and that the activity of a clean platinum surface is arrested by a small quantity of carbon monoxide in the mixture of hydrogen and oxygen. The platinum then recovers its activity when brought into a gas mixture free from carbon monoxide, but when the metal has been " poisoned " by traces of hydrogen sulphide it does not become active again until it has been boiled with concentrated sulphuric acid.

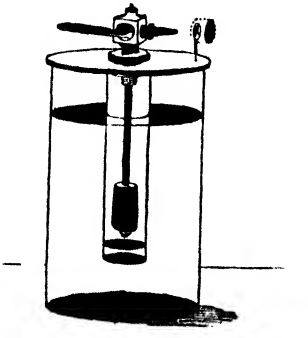


FIG. 87.—Döbereiner's lamp.

Faraday explained his results by a *condensation theory*. He supposed that by the attractive force of the solid the gases " are drawn into association . . . which occasionally leads . . . to the combination of bodies simultaneously subjected to this attraction ".

Fusinieri in 1825 had previously suggested that the platinum " determines upon its surface a continual renovation of concrete layers of the combustible substances, which are burnt, pass away, and are renewed ", which is essentially the same theory.

This *physical theory* suggests that a *film of gas* is condensed on the catalyst surface by molecular attraction and is in a state similar to that of high pressure. Pressure does increase the activity of gases, *e.g.* Beketoff found that hydrogen at 100 atm. pressure displaces silver and mercury from solutions of their salts.

De la Rive in 1838 proposed a *chemical theory* of heterogeneous catalysis, which is an *intermediate compound* theory. Unstable oxides are supposed to be formed on the platinum surface which react with hydrogen in a cyclic manner, the oxide being alternately formed and reduced :

$$2Pt + O_2 = 2PtO$$

$$2H_2 + 2PtO = 2H_2O + 2Pt.$$

The modern view that adsorption is due to *valency forces* acting from the surface atoms seems to reconcile the physical and chemical theories of heterogeneous catalysis.

Graham in 1868 suggested that in gas films formed by *adsorption* on metals the gas molecules are *oriented* in a particular direction, so that the same part of the molecule is always in contact with the metal and the other part exposed as a film to the gas.

Langmuir (1916) has shown that *the adsorbed layer is unimolecular in thickness* and is generally *oriented*, and that " poisoning " is due to the formation of films of molecules on a clean surface which prevent adsorption. In some cases (*e.g.* with carbon monoxide) these films may evaporate again in a pure gas.

Langmuir supposes that the adsorbed molecules are held by chemical forces originating in atoms of metal on the surface. A metal surface is like a chessboard, the black squares being metal atoms and the white the spaces between the atoms. The catalytic action may take place by interaction between molecules or atoms held on adjacent atoms of metal, or between an adsorbed film and the atoms of the solid, or directly as a result of a collision between a gas molecule and a molecule or atom held on the surface. Reaction between hydrogen and oxygen occurs between adjacent adsorbed atoms, that between carbon monoxide and oxygen between adsorbed oxygen atoms and colliding carbon monoxide molecules. The products of reaction evaporate from the surface. Haber (1914) considered that gas molecules are held by electrical forces from the positive and negative ions in the surface of a salt crystal.

tube and the colour matched against a buffer solution of known pH in a comparison tube. In presence of salts and proteins some corrections are necessary (see Clark, *Determination of Hydrogen Ions*; Britton, *Hydrogen Ions*).

(ii) *Gillespie's drop ratio method.*—One tube contains alkali and x drops of a two-colour indicator and another tube acid and $10-x$ drops of indicator. The tubes are superposed and x varied until the tint matches that of a tube of solution of unknown pH and 10 drops of indicator. Then

$$\mathrm{pH} = \mathrm{p}K_a + \log\frac{\alpha}{1-\alpha} = \mathrm{p}K_a + \log\frac{x}{10-x}.$$

E.g. for cresol red $\mathrm{p}K = 8{\cdot}08$, and if $x = 2$, $\mathrm{pH} = 8{\cdot}08 + \log\frac{2}{8} = 7{\cdot}5$.

(iii) *Bjerrum's wedge method.*—In this a glass trough is divided by a vertical glass plate into two equal wedges containing acid and alkaline solutions of a two-colour indicator (Fig. 91). The tint of a given solution and indicator in an equal thickness in a narrow glass cell is matched in the wedge looked at from the side, and if the ratio of acid and alkaline thicknesses in the wedge is x/y this gives the ratio $(1-\alpha) : \alpha$ for the indicator, whence pH is calculated from the formula in (ii).

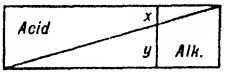


FIG. 91.—Bjerrum's wedge.

An example of a *screened indicator* is a mixture of methyl orange and indigo-carmine which is yellowish-green in alkaline solution and changes through grey at $\mathrm{pH} = 4$ to violet. A *universal indicator* is a mixture of several indicators giving a range of colours for a succession of pH values.

TITRATION CURVES

The plots of the pH values of solutions in acid-alkali titrations against volume of acid or alkali added are called *titration curves*, and are important in giving the pH at the equivalence point and so enabling suitable indicators to be chosen. Some of these curves are shown in Fig. 92.

(1) *Strong acid and strong base.*—Suppose we take 100 c.c. of N HCl and add x c.c. of N NaOH. The un-neutralised acid is $(100-x)$ and the volume $(100+x)$ c.c.; $\therefore$ $[\mathrm{H}^+] = (100-x)/(100+x)$. The $\mathrm{pH} = -\log[\mathrm{H}^+]$ values are :

x	50	75	90	98	99	99·9
pH	0·48	0·85	1·3	2·0	2·3	3·3

For $x = 100$ (equivalence point), $\mathrm{pH} = 7{\cdot}0$, the neutral point, since the acid and base are strong. For x greater than 100 the solution is alkaline. *E.g.* with $x = 100{\cdot}1$, $[\mathrm{OH}^-] = 0{\cdot}1/200{\cdot}1 = 5{\cdot}0 \times 10^{-4}$; $\therefore$ $\mathrm{pOH} = 3{\cdot}3$ and $\mathrm{pH} = 14{\cdot}0 - 3{\cdot}3 = 10{\cdot}7$, since $[\mathrm{H}^+]$ $[\mathrm{OH}^-]$ is always 10^{-14}. There is a very sudden rise in pH as x changes from 99·9 to 100·1, and many suitable indicators may be chosen in the range 3·3 to 10·7.

The second part of the curve is calculated from the values :

x	100·1	100·5	101	110	150	200
pH	10·7	11·4	11·7	12·7	13·3	13·5

Similar curves may be plotted for 0·1*N* and 0·01*N* solutions, when it will be found that the vertical part is shorter and hence there is less choice of indicators. Curves for 0·1*N* solutions are shown in Fig. 92. In this case $[H^{\cdot}] = 0{\cdot}1\,(100 - x)/(100 + x)$ for $x < 100$ and $[OH^{\prime}] = 0{\cdot}1\,(x - 100)/(100 + x)$ for $x > 100$, and it is clear that the pH values are found by adding unity $(-\log 0{\cdot}1)$ to the pH values of *N* solutions given above for $x < 100$, and subtracting unity for values of $x > 100$. The resulting curve is II in Fig. 92.

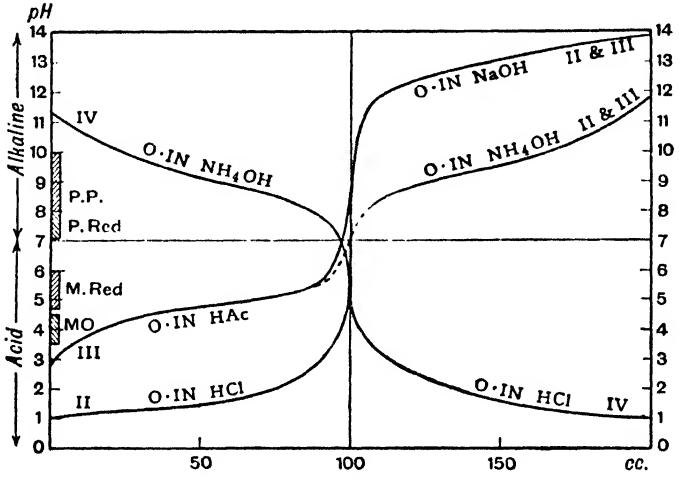


FIG. 92.—Titration curves.

(2) *Weak acid and strong base.*—For the titration of 100 c.c. of 0·1*N* acetic acid with x c.c. of 0·1*N* NaOH we find pH for the equivalence point ($x = 100$) by equation (12) with $K_a = 1{\cdot}82 \times 10^{-5}$ and $c = 0{\cdot}05$:

$$\text{pH} = \tfrac{1}{2}\text{p}K_w + \tfrac{1}{2}\text{p}K_a + \tfrac{1}{2}\log c = 7 + 2{\cdot}37 + \tfrac{1}{2}(-1{\cdot}3) = 8{\cdot}72.$$

For other values of x equation (20) gives :

$$\text{pH} = \text{p}K_a + \log [\text{salt}]/[\text{acid}]. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (20)$$

The initial pH is found from (1) :

$$[H^{\cdot}]\,[Ac^{\prime}]/[HAc] = [H^{\cdot}]^2/0{\cdot}1 = 1{\cdot}82 \times 10^{-5};$$

$$\therefore\ [H^{\cdot}] = \sqrt{1{\cdot}82 \times 10^{-6}} = 1{\cdot}35 \times 10^{-3};\quad \therefore\ \text{pH} = 2{\cdot}87.$$

When x c.c. of 0·1*N* alkali are added, $[\text{salt}] = x \times 0{\cdot}1/(100 + x)$, and

$$[\text{acid}] = (100 - x) \times 0{\cdot}1/(100 + x),$$

from which pH is found from (20). The values are plotted as curve III (Fig. 92). For $x > 100$ it may be assumed that the excess of alkali represses the hydrolysis of the salt, and this part of the curve thus coincides with that of case (1), viz. the alkaline side of curve II.

x -	0	10	25	50	90	99	99·9	100
pH -	2·87	3·8	4·3	4·7	5·7	6·7	7·7	8·87

(3) *Weak base and strong acid.*—For 100 c.c. of $0{\cdot}1N$ NH_4OH ($K_b = 1{\cdot}8 \times 10^{-5}$) with x c.c. of $0{\cdot}1N$ HCl, pH at the equivalence point ($x = 100$) is given by (15) ($c = 0{\cdot}05$) :

$$\text{pH} = \tfrac{1}{2}\text{p}K_w - \tfrac{1}{2}\text{p}K_b - \tfrac{1}{2}\log c = 7 - 2{\cdot}37 - \tfrac{1}{2}(-1{\cdot}3) = 5{\cdot}28,$$

and the initial pH is given by (2) :

$$[NH_4^+][OH']/[NH_4OH] = [OH']^2/0{\cdot}1 = 1{\cdot}8 \times 10^{-5};$$

$$\therefore\ [OH'] = \sqrt{1{\cdot}8 \times 10^{-6}} = 1{\cdot}3 \times 10^{-3};\quad \therefore\ \text{pOH} = 2{\cdot}9;\quad \therefore\ \text{pH} = 14{\cdot}0 - 2{\cdot}9 = 11{\cdot}1.$$

The values for x c.c. of acid are found from (21) :

$$\text{pH} = \text{p}K_w - \text{p}K_b - \log [\text{salt}]/[\text{base}],$$

where $[\text{salt}] = 0{\cdot}1x/(100 + x)$ and $[\text{base}] = 0{\cdot}1(100 - x)/(100 + x)$. The values calculated, and plotted in IV, are :

x	0	10	25	50	90	99	99·9	100
pH	11·1	10·2	9·7	9·3	8·3	7·3	6·3	5·1

After the equivalence point the hydrolysis of the salt is repressed by the hydrochloric acid, and this part of the curve coincides with the acid side of curve II.

(4) *Weak acid and weak base.*—For 100 c.c. of $0{\cdot}1N$ acetic acid ($K_a = 1{\cdot}82 \times 10^{-5}$) titrated with $0{\cdot}1N$ ammonia ($K_b = 1{\cdot}8 \times 10^{-5}$) the equivalence point is given by (19) :

$$\text{pH} = \tfrac{1}{2}\text{p}K_w + \tfrac{1}{2}\text{p}K_a - \tfrac{1}{2}\text{p}K_b = 7{\cdot}0 + 2{\cdot}37 - 2{\cdot}37 = 7 \text{ (neutral point)}.$$

The value of pH at the start is, as calculated in case (2), 2·87. The intermediate values can be calculated over nearly the whole range by (21) and are plotted in curve III, which shows no sudden change in pH, and hence no sharp end-point can be found with any single indicator.

Polybasic acids have separate dissociation constants for each stage of ionisation, *e.g.* phosphoric acid (tribasic) has :

$$[H^+][H_2PO_4']/[H_3PO_4] = K_1 = 8{\cdot}0 \times 10^{-3},$$
$$[H^+][HPO_4'']/[H_2PO_4'] = K_2 = 7{\cdot}4 \times 10^{-8},$$
$$[H^+][PO_4''']/[HPO_4''] = K_3 = 4{\cdot}8 \times 10^{-13}.$$

In such cases the titration curve is formed by superposing the curves plotted for each dissociation separately, provided the dissociation constants are well separated, since each stage of dissociation does not become appreciable until the preceding stage is practically complete. The curves for oxalic acid and carbonic acid in Fig. 93 show that the stages HC_2O_4' and HCO_3' are marked, hence a carbonate can be titrated to the bicarbonate stage with phenolphthalein and completely with methyl orange, but with sulphuric acid the stage HSO_4' does not appear, the pH curve being continuous.

The curve for phosphoric acid is shown in Fig. 94, and it is seen that the end-points for the first two stages, KH_2PO_4 and K_2HPO_4, may be found with suitable indicators, but not the third stage

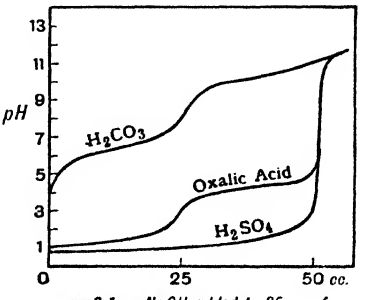


FIG. 93.—Titration curves for dibasic acids.

(K_3PO_4), when the liquid is strongly alkaline. The correct end-point for KH_2PO_4 (or NaH_2PO_4) is when a little orange colour remains with methyl orange, but the next drop of 0·1*N* alkali (not counted) gives a pale yellow; the end-point for Na_2HPO_4 is when the last drop (counted) of 0·1*N* alkali gives a full red colour with phenolphthalein.

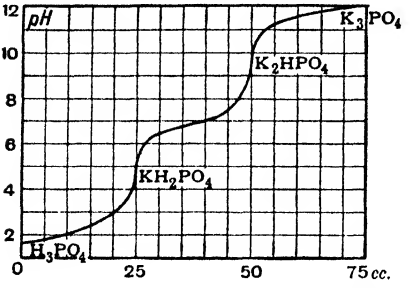


FIG. 94.—Titration curve for phosphoric acid.

THEORY OF ACIDS AND BASES

Whereas most salts are electrovalent compounds (p. 213) containing charged ions even in the solid state, acids and bases are mostly covalent compounds in the pure state and form ions only when dissolved in suitable solvents. Dry liquefied hydrogen chloride does not redden litmus or act on zinc or marble, and is an insulator. In water it behaves as an acid by forming what is called the " hydrogen ion " and usually formulated $H^{\cdot}$; this is probably not the free proton, which could hardly be expected to exist in solution but is solvated to the ion $(H^{\cdot}.H_2O)$ or $H_3O^{\cdot}$ by coordination with a pair of free electrons on the oxygen of the water $H^{+}\leftarrow OH_2$, this ion being really the **hydroxonium ion**, formed similarly to the ammonium ion, which is a coordination of a proton with a pair of electrons on the ammonia nitrogen $H^{+}\leftarrow NH_3$.

Arrhenius pointed out that *all acids form hydrogen ions in solution*, and defined *bases* as *compounds which form hydroxide ions in solution*: $BOH = B^{\cdot} + OH'$. This definition applies strictly only to hydroxides or bases in solution in water, *e.g.* NH_3 was supposed to form NH_4OH which then gave ammonium and hydroxide ions.

An alternative theory proposed by Lapworth (*J.C.S.*, 1908, **93**, 2187) and developed by Lowry (*J.S.C.I.*, 1923, **42**, 43, 1048), Brönsted (*Chem. Rev.*, 1928, **3**, 231), and Bjerrum (*Chem. Rev.*, 1935, **16**, 287; see *Ann. Rep. C.S.*, 1934, **31**, 71) defines an *acid* as a *donor of protons* and a *base* as an *acceptor of protons*. All acids have a common function, but this is not necessary for bases, and in particular they need not produce hydroxide ions, although they usually do so in water by taking up hydrogen ions, *e.g.*:

$$NH_3 + H_2O \rightleftharpoons NH_4^{\cdot} + OH'.$$

The real basic function is combination with an unsolvated hydrogen ion or proton, *e.g.*:

$$NH_3 + H^{\cdot} = NH_4^{\cdot}.$$

Water combines with a proton to form hydroxonium ion:

$$H_2O + H^{\cdot} = H_3O^{\cdot},$$

and is also a base like ammonia, but the greater basic strength of ammonia as compared with water is shown by the alkaline reaction of its solution, *i.e.* the appearance of OH' ions.

The anion of a very weak acid is a strong base, withdrawing hydrogen ions from water to form undissociated acid :

$$CH_3COO' + H^{\cdot} \rightleftharpoons CH_3COOH$$
$$CO_3'' + 2H^{\cdot} \rightleftharpoons H_2CO_3,$$

and leaving the solution alkaline owing to the residual OH' ion of the water. A solution of a salt of the weak acid is thus *hydrolysed*. Hence we can write :

$$\underset{\text{acid}}{HA} \rightleftharpoons \underset{\text{proton}}{H^{\cdot}} + \underset{\text{conjugate base}}{A.} \qquad \text{.....(23)}$$

HA may be a neutral molecule, *e.g.* CH_3COOH, or an ion, *e.g.*

$$NH_4^{\cdot} \rightleftharpoons H^{\cdot} + NH_3,$$

the corresponding conjugate bases being CH_3COO' and NH_3.

A *solvent* B which combines with a proton is a base :

$$HA + B \rightleftharpoons BH^{\cdot} + A,$$

e.g.
$$HA + H_2O \rightleftharpoons H_3O^{\cdot} + A.$$

In anhydrous hydrofluoric acid, nitric acid behaves as a base :

$$HF + HNO_3 \rightleftharpoons H_2NO_3^{\cdot} + F'.$$

The acid reaction of a salt of a weak base is due to dissociation of the ion $BH^{\cdot}$, considered as an acid, into a proton and the conjugate base, *e.g.*

$$NH_4^{\cdot} \rightleftharpoons NH_3 + H^{\cdot}.$$

In aluminium chloride solution the hydrated metal ion functions as a weak acid :

$$(Al(H_2O)_x)^{\cdot\cdot\cdot} \rightleftharpoons Al(H_2O)_{x-1}(OH)^{\cdot\cdot} + H^{\cdot}.$$

Multivalent positive ions ($Al^{\cdot\cdot\cdot}$, $Cu^{\cdot\cdot}$, $Zn^{\cdot\cdot}$, $Cd^{\cdot\cdot}$, $Hg^{\cdot\cdot}$, $Pb^{\cdot\cdot}$) which have strong attractions for negative OH' ions behave in this way. Other bivalent ($Ba^{\cdot\cdot}$, etc.), and univalent ($K^{\cdot}$, etc.), cations do not so function. In some cases the metal hydroxide is precipitated and hydrogen ions from the water appear, *e.g.* $[Sn(H_2O)_x]^{\cdot\cdot\cdot\cdot}$ does not exist in solution but forms $Sn(OH)_4$, and in hydrochloric acid $SnCl_6''$.

The *hydrolysis of salts of weak bases* is easily explained on the new theory (cf. p. 152). The basic dissociation constant of ammonia,

$$NH_3 + H_2O \rightleftharpoons NH_4^{\cdot} + OH',$$

is
$$K_b = [NH_4^{\cdot}]\,[OH']/[NH_3],$$

and the acid dissociation constant of the ammonium ion $NH_4^{\cdot} \rightleftharpoons NH_3 + H^{\cdot}$ is

$$K_a = [NH_3]\,[H^{\cdot}]/[NH_4^{\cdot}].$$

Hence
$$K_aK_b = [H^{\cdot}]\,[OH'] = K_w. \qquad \text{.....(24)}$$

This is quite general : *the dissociation constant of a weak acid is inversely proportional to the dissociation constant of its conjugate base.*

In a solution 0·01 molar in ammonia and 0·02 molar in NH_4Cl, the ammonium ion $[NH_4^+] = 0{\cdot}02$ is the acid with $K_a = 3{\cdot}3 \times 10^{-10}$, and ammonia $[NH_3] = 0{\cdot}01$ is the conjugate base. Hence

$$[H^+] = K_a[NH_4^+]/[NH_3] = 3{\cdot}3 \times 10^{-10} \times 0{\cdot}02/0{\cdot}01 = 6{\cdot}6 \times 10^{-10}.$$

For a salt of a weak acid and excess of acid anion as conjugate base, (23) gives

$$[H^+][A]/[HA] = K_a,$$

$$\therefore\ [H^+] = K_a[HA]/[A] = K_a\frac{[\text{acid}]}{[\text{base}]}, \quad \ldots\ldots\ldots\ldots\ldots\ldots(25)$$

which is equivalent to formula (20) for a buffer solution when [salt] = [base], the salt being practically completely ionised.

In a solution 0·05 molar in sodium acetate and 0·02 molar in acetic acid, the acid is acetic acid with $K_a = 1{\cdot}8 \times 10^{-5}$ and the conjugate base the acetate ion,

$$\therefore\ [H^+] = 1{\cdot}8 \times 10^{-5} \times 0{\cdot}02/0{\cdot}05 = 7{\cdot}2 \times 10^{-6}.$$

For a solution of a base A which develops an alkaline reaction we may modify (23) to :

$$\underset{\text{base}}{A} + H_2O \rightleftharpoons \underset{\text{acid}}{HA} + OH',$$

$$\therefore\ K_b = [HA]\,[OH']/[A].$$

Since in a solution of pure base, OH′ and acid are produced in equal amounts :

$$K_b = [OH']^2/[\text{base}] = K_w/K_a \text{ from (24)};$$

$$\therefore\ [H^+] = K_w/[OH'] = \sqrt{K_aK_w/[\text{base}]}. \quad \ldots\ldots\ldots\ldots\ldots\ldots(26)$$

We see that in this case K_b is the same as the hydrolysis constant (p. 152).

In 0·05 molar sodium acetate the base is the acetate ion,

$$\therefore\ [\text{base}] = 0{\cdot}05,\ K_a = 1{\cdot}8 \times 10^{-5} \quad \text{and} \quad K_w = 10^{-14} \text{ at } 25°;$$

$$\therefore\ [H^+] = \sqrt{1{\cdot}8 \times 10^{-5} \times 10^{-14}/0{\cdot}05} = 1{\cdot}9 \times 10^{-9}.$$

Non-aqueous solutions.—The strength of an acid depends on the solvent. In water, the tendency of the proton to form the H_3O^+ ion is so great that most strong acids are equally strong in water, which is an example of a *levelling solvent*. In solvents such as benzene, if the acid dissolves, it is mostly in the covalent state, as the solvent molecules have no tendency to combine with protons. In acetic acid the tendency to combine with a proton is small, since acetic acid is a very weak acid and even the very strong perchloric acid is little ionised. In solution in stronger acids (*e.g.* hydrofluoric) other acids may function as bases (p. 163). In methyl and ethyl alcohols, nitric acid is weaker than perchloric acid, although both are equally strong in water, and in nitrobenzene perchloric acid is moderately strong and nitric acid very weak.

The theory of acids and bases has been extended to include reactions in non-aqueous solvents (Hall, *Chem. Rev.*, 1931, **8**, 191 ; Luder, *ibid.*, 1940, **27**, 547).

(i) In the **solvent-system** theory (based on Franklin's work, p. 548) *an acid is a solute forming a cation characteristic of the solvent* (H_3O^+ in water and NH_4^+ in

anhydrous liquid ammonia), *a base is a solute forming an anion characteristic of the solvent* (OH' in water and NH_2' in ammonia: $2NH_3 \rightleftharpoons NH_4^{\cdot} + NH_2'$), and neutralisation is formation of solvent molecules:

$$(H_3O)Cl + NaOH = NaCl + 2H_2O$$
$$\underset{\text{acid}}{NH_4Cl} + \underset{\text{base}}{NaNH_2} = \underset{\text{salt}}{NaCl} + \underset{\text{solvent}}{2NH_3}.$$

(ii) G. N. Lewis defines *acids* as *substances which, like hydrogen ion, neutralise hydroxide ion or any other base*, and *bases* as *substances which, like hydroxide ion, neutralise hydrogen ion or any other acid.* He recognises acidic and basic properties in various solvents by means of indicators and "neutralisation" by appropriate indicator colour. Then triethylamine NEt_3 ($Et = C_2H_5$) is found to be a base and BCl_3, $SnCl_4$, etc., are "acids". The *acids* are then found to be *substances which can accept electron pairs* to form coordinate links (p. 213), and *bases* are *substances which can donate electron pairs*; neutralisation, in the absence of a solvent or in an indifferent solvent, involves the formation of a covalent link.

Lewis classifies acids and bases into (i) *primary*, when combination occurs practically without energy of activation (p. 142), and (ii) *secondary*, when neutralisation is slow (*e.g.* with CO_2) and requires energy of activation; the normal molecule, which is not an electron-pair acceptor, becomes one by electronic rearrangement by resonance (p. 269).

Amphoteric electrolytes.—Some metal hydroxides can act either as weak bases (in presence of strong acids) or as weak acids (in presence of strong bases). Zinc hydroxide forms zinc salts with acids and zincates with alkalis, and this may be explained by alternative ionisations:

$$\underset{\text{acid function}}{2H^{\cdot} + ZnO_2''} \rightleftharpoons Zn(OH_2) \rightleftharpoons \underset{\text{base function}}{Zn'' + 2OH'}.$$

Electrolytes which act both as *weak* bases and *weak* acids are called *amphoteric electrolytes* or *ampholytes.*

An important group comprises the amino-acids such as glycine (aminoacetic acid), which in solution probably exist mostly as an *amphion* (or *hybrid ion*, p. 156) having both positive and negative charges, and this is indicated by the crystal structure of glycine:

$$NH_2 \cdot CH_2 \cdot COOH \rightleftharpoons \overset{+}{N}H_3 \cdot CH_2 \cdot \overset{-}{C}OO.$$

If a strong acid is added the proton neutralises the carboxyl $\overset{-}{C}OO$ group:

$$\overset{+}{N}H_3 \cdot CH_2 \cdot \overset{-}{C}OO + H^{\cdot} \rightleftharpoons \overset{+}{N}H_3 \cdot CH_2 \cdot COOH, \quad \text{.....(A)}$$

whilst a strong base, *e.g.* hydroxide ion, removes a proton from the $\overset{+}{N}H_3$ group:

$$\overset{+}{N}H_3 \cdot CH_2 \cdot \overset{-}{C}OO + OH' \rightleftharpoons NH_2 \cdot CH_2 \cdot \overset{-}{C}OO + H_2O. \quad \text{.....(B)}$$

Equation (A) reversed represents the acidic function of the carboxylic acid of which the amphion is the conjugate base:

$$\overset{+}{N}H_3 \cdot CH_2 \cdot COOH + H_2O \rightleftharpoons \overset{+}{N}H_3 \cdot CH_2 \cdot \overset{-}{C}OO + H_3O^{\cdot},$$

and equation (B) reversed represents the basic function of the amine base of which the substituted ammonium ion is the conjugate acid :

$$NH_2 \cdot CH_2 \cdot \overset{-}{C}OO + H_2O \rightleftharpoons \overset{+}{N}H_3 \cdot CH_2 \cdot \overset{-}{C}OO + OH'.$$

The acid and base dissociation constants are :

$$K_a = [H^+]\,[\overset{+}{N}H_3 \cdot CH_2 \cdot \overset{-}{C}OO]/[\overset{+}{N}H_3 \cdot CH_2 \cdot COOH] = 10^{-2\cdot33}$$

$$K_b = [\overset{+}{N}H_3 \cdot CH_2 \cdot \overset{-}{C}OO]\,[OH']/[NH_2 \cdot CH_2 \cdot \overset{-}{C}OO] = 10^{-4\cdot15}.$$

Strong Electrolytes

The law of mass action does not apply to strong electrolytes, which are considered to be completely ionised in dilute solutions. In more concentrated solutions ion pairs are formed, but these are not true covalent molecules like those of weak electrolytes. Hence an equation similar to (1) does not apply to, say, potassium chloride, as the following figures show, α being assumed to be given by λ/λ_∞ :

$c = 1/V$ mols per lit. -	10^{-5}	10^{-3}	10^{-1}	1
$\alpha = \lambda/\lambda_\infty$ - - -	0·994	0·980	0·862	0·757
$K = \alpha^2 c/(1-\alpha)$ - -	0·0016	0·048	0·55	2·36

We now believe that $\alpha = 1$ throughout and K has no meaning, since α is not given by λ/λ_∞ (p. 110).

G. N. Lewis introduced the useful idea of the *activity* of a solute, this being a quantity a which plays the same part as the concentration c in ideal solutions (obeying the gas laws) and is equal to c at infinite dilution. Thus for a strong electrolyte giving two univalent ions: $MA = M^+ + A'$, we may define the activities by the equation :

$$a_+ a_- = a^2, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (27)$$

where a_+, a_- are the activities of the ions, a the mean activity of the electrolyte. The ratio a/c is called the *activity coefficient* f :

$$a/c = f, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (28)$$

which varies with the concentration of the ions; at infinite dilution the value of f is unity. Hence :

$$(f_+ c_+)(f_- c_-) = fc \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (29)$$

where f is the activity coefficient of the electrolyte of concentration c.

The activity coefficients of the ions depend on the *total* ion concentration, including ions of other salts present. For a solid salt in equilibrium with its saturated solution, the activity of the dissolved salt is constant at a given temperature, but it is found that the solubility c increases if another salt having no ions in common with the first is present in solution. Since fc is constant it follows that f must vary. Debye and Hückel in 1923 showed that the activity

coefficient of a given salt (electrolyte) in very dilute solution in water at 25° is given by:

$$\log f = 0{\cdot}5 z_+ z_- \sqrt{I}, \quad \ldots\ldots(30)$$

where I is the *ionic strength*:

$$I = \tfrac{1}{2}\Sigma c_i z_i^2, \quad \ldots\ldots(31)$$

and depends on the concentrations c_i and valencies z_i of *all* the ions in solution. In (30) z_+ and z_- are the valencies of the ions of the given salt with proper signs ($z_+ z_-$ is negative).

For an electrolyte giving multivalent ions:

$$X = \nu_+ X^+ + \nu_- X^-,$$

where ν_+ and ν_- are the numbers of ions, we have

$$c_+^{\nu+} f_+^{\nu+} \cdot c_-^{\nu-} f_-^{\nu-} = a^\nu, \quad \ldots\ldots(32)$$

where $\nu = \nu_+ + \nu_-$, a is the activity, and the activity coefficient is defined as the geometric mean of the activity coefficients of the ions:

$$f = (f_+^{\nu+} f_-^{\nu-})^{\frac{1}{\nu}}. \quad \ldots\ldots(33)$$

For a completely ionised electrolyte giving univalent ions:

$$c_+ = c_- = c, \text{ the total concentration;}$$
$$\therefore\ I = \tfrac{1}{2}\Sigma c_i z_i^2 = \tfrac{1}{2}(c_+ + c_-) = \tfrac{1}{2}(2c) = c,$$

i.e. the ionic strength is equal to the total concentration. Hence the activity coefficient of 0·01 N KCl at 25° is given by:

$$\log f = 0{\cdot}5 z_+ z_- \sqrt{I}$$
$$= -0{\cdot}5\sqrt{0{\cdot}01}$$
$$= -0{\cdot}05 = -1 + 0{\cdot}95;$$
$$\therefore\ f = \text{antilog}(\bar{1}{\cdot}95) = 0{\cdot}891.$$

For completely ionised barium chloride in 0·01 molar solution at 25° ($Ba^{\cdot\cdot} + 2Cl'$), $c_+ = c$, $c_- = 2c$, $z_+ = 2$, $z_- = -1$;

$$\therefore\ I = \tfrac{1}{2}(2^2 c + (-1)^2 2c) = 3c = 0{\cdot}03,$$
$$\therefore\ \sqrt{I} = 0{\cdot}173,$$
$$\therefore\ \log f = 0{\cdot}5 z_+ z_- \sqrt{I} = 0{\cdot}5 \times 2 \times (-1) \times 0{\cdot}173 = -0{\cdot}173$$
$$= \bar{1}{\cdot}827,$$
$$\therefore\ f = \text{antilog}\,\bar{1}{\cdot}827 = 0{\cdot}67.$$

In a solution containing 0·01 molar KCl and 0·01 molar $BaCl_2$, completely ionised, at 25°:

$$c_{K^\cdot} = 0{\cdot}01, \quad c_{Ba^{\cdot\cdot}} = 0{\cdot}01, \quad c_{Cl'} = 0{\cdot}02 + 0{\cdot}01 = 0{\cdot}03;$$
$$\therefore\ I = \tfrac{1}{2}(0{\cdot}01 \times 1^2 + 0{\cdot}01 \times 2^2 + 0{\cdot}03 \times (-1)^2) = 0{\cdot}04.$$

The activity coefficient of the potassium chloride is given by:

$$\log f = 0{\cdot}5 z_+ z_- \sqrt{I} = 0{\cdot}5 \times 1 \times (-1)\sqrt{0{\cdot}04} = -0{\cdot}1; \quad \therefore\ f = 0{\cdot}79;$$

and the activity coefficient of the barium chloride is given by:

$$\log f = 0{\cdot}5 z_+ z_- \sqrt{I} = 0{\cdot}5 \times 2 \times (-1)\sqrt{0{\cdot}04} = -0{\cdot}2; \quad \therefore\ f = 0{\cdot}63.$$

Solubility Product

In a very dilute saturated solution of a strong electrolyte BA in pure water the substance is assumed to be completely ionised: $BA = B^+ + A^-$, and if S_0 is the solubility of BA in mols per litre, $S_0 = [B^+]_0 = [A^-]_0$, *i.e.* equal to each separate ion concentration. Hence the ionic concentration product is

$$[B^+]_0[A^-]_0 = S_0^2. \quad \ldots\ldots(34)$$

This is called the **solubility product,** K_s, and for any solute and solvent it depends on the temperature.

If another salt, say CA, having a common ion, say A^-, is added to the saturated solution of BA, the **solubility product principle** states that the ionic concentration product of BA still has the same value:

$$[B^+][A^-] = [B^+]_0[A^-]_0 = S_0^2. \quad \ldots\ldots(35)$$

Since $[A^-]$ has increased, $[B^+]$ must have decreased, and this can only occur by some salt BA going out of solution. The solubility of BA is, therefore, decreased to S, where $S < S_0$. Since the values of $[A^-]$ and S_0 are known, that of $[B^+]$ may be calculated, and as $[B^+]$ is equal to the total concentration S of completely ionised BA, the value of S may be calculated.

For an electrolyte B_pA_q giving p positive ions and q negative ions, the solubility product is $[B^+]^p[A^-]^q = \text{const.}$

Expt. 2. To a saturated solution of silver acetate add (*a*) concentrated silver nitrate, (*b*) saturated sodium acetate, solutions. In both cases silver acetate is precipitated.

The *solubility products* K_s of common precipitates are given below for room temperature (25°) (some alternative values are in brackets):

$[Ag^+][Cl^-]$	$1{\cdot}2 \times 10^{-10}$	$[Ca^{++}][CO_3^{--}]$	$7{\cdot}2 \times 10^{-9}$	$[Fe^{++}][OH^-]^2$	$1{\cdot}6 \times 10^{-14}$
$[Ag^+][Br^-]$	$3{\cdot}5 \times 10^{-13}$	$[Ca^{++}][SO_4^{--}]$	$2{\cdot}3 \times 10^{-4}$	$[Fe^{+++}][OH^-]^3$	$1{\cdot}1 \times 10^{-36}$
$[Ag^+][I^-]$	$1{\cdot}7 \times 10^{-16}$	$[Ca^{++}][C_2O_4^{--}]$	$3{\cdot}8 \times 10^{-9}$	$[Mg^{++}][OH^-]^2$	$2{\cdot}5 \times 10^{-13}$
$[Ag^+][CNS^-]$	$7{\cdot}1 \times 10^{-13}$	$[Cu^+][I^-]$	$2{\cdot}6 \times 10^{-12}$	$[Mn^{++}][OH^-]^2$	$4{\cdot}0 \times 10^{-14}$
$[Ba^{++}][SO_4^{--}]$	$1{\cdot}2 \times 10^{-10}$	$[Cu^+][CNS^-]$	$1{\cdot}7 \times 10^{-11}$	$[Pb^{++}][SO_4^{--}]$	$2{\cdot}3 \times 10^{-8}$
				$[Pb^{++}][CrO_4^{--}]$	$1{\cdot}8 \times 10^{-14}$

$[Mn^{++}][S^{--}]$	$1{\cdot}4 \times 10^{-15}$	$[Cd^{++}][S^{--}]$	$3{\cdot}6 \times 10^{-29}$
$[Fe^{++}][S^{--}]$	$1{\cdot}5 \times 10^{-19}$	$[Cu^{++}][S^{--}]$	$8{\cdot}5 \times 10^{-44}$ ($8{\cdot}5 \times 10^{-42}$)
$[Zn^{++}][S^{--}]$	$1{\cdot}0 \times 10^{-20}$ (1×10^{-29}; $1{\cdot}5 \times 10^{-26}$)	$[Cu^+]^2[S^{--}]$	2×10^{-47} ($3{\cdot}6 \times 10^{-50}$)
$[Ni^{++}][S^{--}]$	$1{\cdot}4 \times 10^{-24}$ ($1{\cdot}1 \times 10^{-27}$)	$[Ag^+]^2[S^{--}]$	$1{\cdot}6 \times 10^{-49}$
$[Co^{++}][S^{--}]$	3×10^{-26} ($1{\cdot}9 \times 10^{-27}$)	$[Hg^{++}][S^{--}]$	4×10^{-52}
$[Pb^{++}][S^{--}]$	5×10^{-29} (7×10^{-30})		

Example 1.—Calculate the solubility of silver chloride at 25°. Since the solubility is small, the silver chloride is almost completely ionised, hence if the solubility is S mols per lit.

$$[Ag^+] = [Cl^-] = S; \quad \therefore\ S^2 = K_s;$$

$$\therefore\ S = \sqrt{K_s} = \sqrt{1{\cdot}2 \times 10^{-10}} = 1{\cdot}095 \times 10^{-5} \text{ mols per lit.}$$

EXAMPLE 2.—Solid silver chloride is shaken with 1 lit. of sodium chloride solution containing 3 g. of the salt. If the solubility product of AgCl at the temperature of the experiment is 9×10^{-11} and the NaCl is completely ionised, how many g. of AgCl will dissolve?

3 g. of NaCl $= 3/58{\cdot}5 = 5{\cdot}13 \times 10^{-2}$ mols; $\therefore$ [Cl′] from NaCl $= 5{\cdot}13 \times 10^{-2}$ mols/lit. Let x mols of AgCl dissolve. This forms x mols of $Ag^{\cdot}$ and Cl′, since it is assumed completely ionised. Hence in the solution $[Ag^{\cdot}] = x$ and $[Cl'] = 5{\cdot}13 \times 10^{-2} + x$; $\therefore\ x(x + 5{\cdot}13 \times 10^{-2}) = K_s = 9 \times 10^{-11}$. Since x^2 may be neglected in comparison with x, $5{\cdot}13 \times 10^{-2}x = 9 \times 10^{-11}$. $\therefore\ x = 1{\cdot}75 \times 10^{-9}$ mols/lit., or

$$1{\cdot}75 \times 10^{-9} \times 143{\cdot}38 = 2{\cdot}5 \times 10^{-7} \text{ g./lit.}$$

In very dilute solutions the solubility product principle gives satisfactory results, as is seen from the following figures (concentrations in mols per litre) for silver nitrite.

Conc. of $AgNO_3$ or KNO_2.	Solubility of $AgNO_2$ in presence of		Solubility calcd.
	$AgNO_3$.	KNO_2.	
0	0·0269	0·0269	0·0269
0·00258	0·0260	0·0259	0·0257
0·00588	0·0244	0·0249	0·0241
0·02355	0·0192	0·0203	0·0176

In such dilute solutions the activity coefficients are practically unity, so that the principle, which holds strictly only for activities, will hold very closely for concentrations:

$$a_+^{\,p} a_-^{\,q} = c_+^{\,p} f_+^{\,p} \,.\, c_-^{\,q} f_-^{\,q} \simeq c_+^{\,p} c_-^{\,q} = \text{const.}$$

An important application of the solubility product is in the **precipitation of sulphides of metals** in qualitative analysis. A saturated solution of hydrogen sulphide at 25° is about 0·1 molar. The first and second dissociation constants (p. 149) are:

$$[H^{\cdot}][HS']/[H_2S] = 9{\cdot}1 \times 10^{-8} \quad \text{and} \quad [H^{\cdot}][S'']/[HS'] = 1{\cdot}2 \times 10^{-15}.$$

With $[H_2S] = 0{\cdot}1$ and $[H^{\cdot}] = [HS']$ (neglecting the very small ionisation of HS′),

$$[H^{\cdot}] = [HS'] = \sqrt{9{\cdot}1 \times 10^{-8} \times 0{\cdot}1} = 9{\cdot}5 \times 10^{-5},$$

hence $$[S''] = 1{\cdot}2 \times 10^{-15} \times 9{\cdot}5 \times 10^{-5}/9{\cdot}5 \times 10^{-5} = 1{\cdot}2 \times 10^{-15}.$$

In 0·25 molar HCl (assumed completely dissociated) the solubility of H_2S is approximately the same as in water, but the ion concentrations are much reduced. We now have $[H^{\cdot}] = 0{\cdot}25$,

$$\therefore\ [HS'] = 9{\cdot}1 \times 10^{-8}\,[H_2S]/[H^{\cdot}] = 9{\cdot}1 \times 10^{-8} \times 0{\cdot}1/0{\cdot}25 = 3{\cdot}6 \times 10^{-8}$$

and $$[S''] = 1{\cdot}2 \times 10^{-15}\,[HS']/[H^{\cdot}] = 1{\cdot}2 \times 10^{-15} \times 3{\cdot}6 \times 10^{-8}/0{\cdot}25 = 1{\cdot}7 \times 10^{-22}.$$

The solubility product of ZnS is $1{\cdot}0 \times 10^{-20}$; $\therefore$ in 0·1 molar solution of a zinc salt (assumed completely ionised) in a saturated solution of hydrogen

sulphide in water $[Zn^{\cdot\cdot}]\,[S'']=0{\cdot}1\times1{\cdot}2\times10^{-15}=1{\cdot}2\times10^{-16}$. This is greater than the solubility product, hence some ZnS is precipitated. The precipitation is incomplete, because the accumulation of hydrogen ions from the reaction $Zn^{\cdot\cdot}+H_2S=ZnS+2H^{\cdot}$ reduces the value of $[S'']$ by mass action below that corresponding with $[Zn^{\cdot\cdot}]\,[S'']=1{\cdot}0\times10^{-20}$. In a solution of H_2S in 0·25 molar HCl, $[S'']=1{\cdot}7\times10^{-22}$, and if it is 0·1 molar in zinc,

$$[Zn^{\cdot\cdot}]\,[S'']=0{\cdot}1\times1{\cdot}7\times10^{-22}=1{\cdot}7\times10^{-23},$$

which is below the solubility product, hence zinc sulphide is not precipitated.

The solubility products of CuS, HgS, PbS and CdS are much smaller than $1{\cdot}7\times10^{-23}$, hence these are precipitated in the acid solution. If sodium acetate is added, or ammonium sulphide in alkaline solution is used as a precipitant, the value of $[H^{\cdot}]$ is kept low, hence $[S'']$ increases and the solubility products of ZnS, MnS, etc., are exceeded, and these are precipitated.

EXAMPLE 3.—Calculate the *maximum* concentrations of $Cd^{\cdot\cdot}$ and $Mn^{\cdot\cdot}$ in a solution containing 0·25 molar HCl and saturated with H_2S.

$[S'']$ in the solution is $1{\cdot}7\times10^{-22}$ mol/lit., and the solubility products are $[Cd^{\cdot\cdot}]\,[S'']=3{\cdot}6\times10^{-29}$; $[Mn^{\cdot\cdot}]\,[S'']=1\,4\times10^{-15}$. Hence :

$$[Cd^{\cdot\cdot}]=3{\cdot}6\times10^{-29}/1{\cdot}7\times10^{-22}=2{\cdot}1\times10^{-7}\text{ mol/lit.},$$

which is only $2{\cdot}1\times10^{-7}\times112{\cdot}4=2{\cdot}4\times10^{-5}$ g./lit., so that cadmium would be precipitated.

$$[Mn^{\cdot\cdot}]=1{\cdot}4\times10^{-15}/1{\cdot}7\times10^{-22}=8{\cdot}2\times10^{6}\text{ mol/lit., or}$$

$8{\cdot}2\times10^{6}\times55=4{\cdot}5\times10^{8}$ g./lit., hence no manganese would be precipitated.

The *solubility of metallic sulphides, etc., in acids* may be explained on similar grounds. A trace of sulphide is soluble in water and ionises : *e.g.* $FeS\rightleftharpoons Fe^{\cdot\cdot}+S''$, and its sulphide ion S'' combines with the hydrogen ion of the acid to form the weakly ionised H_2S : $S''+2H^{\cdot}\rightleftharpoons H_2S$. Then more sulphide dissolves. If it is one of the more soluble sulphides (*e.g.* FeS, ZnS, MnS), its solubility product is not exceeded even in acid saturated with H_2S, so that this escapes as gas and the sulphide dissolves as long as acid is present. With very sparingly soluble sulphides (*e.g.* PbS, CuS), the solubility product is exceeded before the solution is saturated with H_2S and the sulphide is not dissolved.

Complex ions.—Silver chloride dissolves in ammonia to form the complex ion $Ag(NH_3)_2^{\cdot}$, and silver cyanide dissolves in alkali cyanide solution to form the complex ion $Ag(CN)_2'$. *A complex ion is formed by the combination of a simple ion with neutral molecules or other ions of opposite charge.* The stability of a complex ion may vary considerably.

The complex ion $Ag(CN)_2'$ is slightly dissociated :

$$Ag(CN)_2'\rightleftharpoons Ag^{\cdot}+2CN',$$

but the silver ion concentration is so small that it is not precipitated by chlorides (solubility product $[Ag^{\cdot}]\,[Cl']=1{\cdot}2\times10^{-10}$), although it is precipitated by sulphides (solubility product $[Ag^{\cdot}]^2[S'']=1{\cdot}6\times10^{-49}$).

The dissociation of a complex ion is measured by the *instability constant*:

$[Ag^+][NH_3]^2/[Ag(NH_3)_2^+] = 6{\cdot}8 \times 10^{-8}$. $[Cd^{++}][CN^-]^4/[Cd(CN)_4^{--}] = 1{\cdot}4 \times 10^{-17}$.

$[Ag^+][S_2O_3^{--}]^2/[Ag(S_2O_3)_2^{---}] = 1{\cdot}0 \times 10^{-13}$.

$[Ag^+][CN^-]^2/[Ag(CN)_2^-] = 1{\cdot}0 \times 10^{-21}$. $[Hg^{++}][I^-]^4/[HgI_4^{--}] = 5{\cdot}0 \times 10^{-31}$.

$[Cu^+][CN^-]^4/[Cu(CN)_4^{---}] = 5{\cdot}0 \times 10^{-28}$. $[Hg^{++}][CN^-]^4/[Hg(CN)_4^{--}] = 4{\cdot}0 \times 10^{-42}$.

In the separation of copper and cadmium, hydrogen sulphide is passed into a solution containing $Cu(CN)_4^{---}$ and $Cd(CN)_4^{--}$ in presence of a small excess of alkali cyanide. The cuprous ion concentration from the $Cu(CN)_4^{---}$:

$$Cu(CN)_4^{---} \rightleftharpoons Cu^+ + 4CN^-$$

is too small to exceed the solubility product of Cu_2S, but the cadmium ion concentration from the less stable $Cd(CN)_4^{--}$: $Cd(CN)_4^{--} \rightleftharpoons Cd^{++} + 4CN^-$, is large enough to exceed the solubility product of CdS and this is precipitated (see the full calculation in Partington and Stratton, *Intermediate Chemical Calculations*, Chap. XII).

Methods used for the detection of complex ions and in some cases the determination of their formulae include:

(1) *Abnormal solubilities.*—Silver cyanide dissolves in potassium cyanide solution and the composition of saturation is approximately AgCN : KCN, hence the complex ion is probably $Ag(CN)_2^-$.

(2) *Distribution coefficient.*—Ammonia is extracted from water solution by chloroform, and from the composition of the chloroform layer and the distribution coefficient (p. 58) the NH_3 concentration in the water is found. Cupric hydroxide dissolves in ammonia to form a deep blue solution, and from the distribution ratio with chloroform the concentration of *free* ammonia in the solution is calculated. The remainder is combined with the copper, and thence the composition of the complex ion is calculated as $Cu(NH_3)_4^{++}$ (Dawson and McCrae, *J.C.S.*, 1900, **77**, 1239; 1901, **79**, 1072).

(3) The *freezing-point depression* gives the total number of particles, ions and molecules, in a solution. On adding iodine to potassium iodide solution the freezing point is unchanged, hence the reaction is $K^+ + I^- + nI_2 = K^+ + I(nI_2)^-$. Method (2) shows that $n = 1$ and the ion is I_3^-. Similarly the aluminate ion is found to be AlO_2^-: $Al(OH)_3 + OH^- = AlO_2^- + 2H_2O$.

(4) *Abnormal transport numbers* (p. 105) indicate the formation of complex anions from metal cations, *e.g.* in concentrated CdI_2 solution part of the cadmium travels to the *anode*, because the ion CdI_4^{--} is present.

(5) *Conductivity changes* indicate the increase or decrease of the number of ions in solution and sometimes the formation of complex ions can be detected.

(6) *Electromotive force* measurements will sometimes decide the formula of a complex ion $M_qA_r \rightleftharpoons qM^{+} + rA^{-}$ by measurement of the metal ion concentration $[M^+]$ from electrode potentials (p. 116), and variation of the concentration of the solution and of the concentration of a salt with a common ion A^-. This method has been used with complex cyanides.

CHAPTER VII

THE PERIODIC LAW

Prout's hypothesis.—The idea that all elements are formed from one primary substance is found in old Greek philosophy. Sir H. Davy in 1812 suggested that the " undecompounded substances " are compounds of hydrogen " with another principle as yet unknown in the separate form ", and that " the same ponderable matter in different electrical states, or in different arrangements, may constitute substances chemically different ". Dr. William Prout in 1815 concluded that *the atomic weights of the elements are whole multiples of that of hydrogen*, and in 1816 he suggested that *the atoms of all elements are formed by the condensation of atoms of hydrogen*, so that hydrogen is the primary substance or *protyle* (Greek *prote*, first ; *hulé*, matter).

Although Prout's hypothesis was soon disproved by more accurate atomic weight determinations of Berzelius, Turner and others, it still fascinated chemists. Dumas and Stas in 1841 showed that the atomic weight of carbon was almost exactly 12 and that Berzelius's value was 2·5 p.c. in error, and in 1842 they found that the atomic weight of oxygen (on the standard H = 1) is almost exactly 16, which again seemed to support Prout's hypothesis. The general accuracy of Berzelius's other results was later confirmed and it was clear that Prout's hypothesis was unacceptable in its original form.

The atomic weight of chlorine is close to 35·5, so that Marignac suggested that atomic weights are multiples of half the atomic weight of hydrogen, and Dumas later reduced this to a quarter, but this was obviously very arbitrary. Stas, beginning with " an almost complete confidence in the exactness of the law of Prout ", was led by his exact researches to assert in 1860 that it is " a pure illusion ", a hypothesis definitely contradicted by experiment, and it was also rejected by Mendeléeff. Marignac, in a comment on Stas's paper, however, suggested that " while preserving the fundamental principle of . . . the hypothesis of the unity of matter ", we might " suppose that the cause which has determined certain groupings of the atoms of the sole primordial substance " may have exercised an influence such that " the weight of each group might not be exactly the sum of the weights of the primordial atoms composing it ". In many cases also the atomic weights are so nearly whole numbers " that it is impossible to consider this fact as accidental " (*Alembic Club Reprint*, 1932, **20**).

Crookes in 1886, as a result of experiments, concluded that in the discharge of electricity in gases at very low pressures, the electricity is carried by particles of a " fourth state of matter " (*cathode rays*) much more subtle than the gaseous. He identified this with protyle (which he derives from *pro*, earlier than, and *hulé*), and supposed that the atoms are condensations of it (*Chem. News*, 1886, **54**, 115 ; *Nature*, 1886, **34**, 423) ; his " cathode rays " were free electrons (p. 184). He also supposed, like Marignac, that all the atoms of a given element might not be identical : " our atomic weights merely represent a mean value

around which the actual atomic weights of the atoms vary within certain narrow limits "—a striking anticipation of isotopes.

The law of triads.—Döbereiner (the chemical teacher of Goethe) noticed in 1817 that the atomic weight of strontium is approximately the mean of those of calcium and barium, and in 1829 he extended this **law of triads** to other elements :

Ca 40	Sr 88	Ba 137
S 32	Se 79	Te 128
Cl 35·5	Br 80	I 127

Lenssen in 1857 tried to arrange all the elements in triads, and attempts to find numerical regularities among atomic weights were also made between 1850 and 1859 by Pettenkofer, Kremers, Gladstone, Dumas, Cooke, Odling, and others, that of Odling being very similar to the later periodic table.

The law of octaves.—De Chancourtois in 1862 (Hartog, *Nature*, 1889, **41**, 186) arranged the elements in the order of their atomic weights in a spiral around a cylinder divided into vertical strips. He found that similar elements fall on the same vertical of this *vis tellurique* or *De Chancourtois helix*. His work attracted no attention, although spiral arrangements of the periodic system were afterwards devised by Crookes (*Proc. Roy. Soc.*, 1898, **63**, 408) and Harkins and Hall (*J.A.C.S.*, 1916, **38**, 169). An interesting form is the logarithmic spiral proposed by G. Johnstone Stoney (*Chem. News*, 1888, **57**, 163 ; *Phil. Mag.*, 1909, **4**, 411, 504).

Newlands in 1864 noticed that if the elements are arranged in the order of the atomic weights as given by Cannizzaro (1858) "the eighth element, starting from a given one is a kind of repetition of the first, like the eighth note in an octave of music ", and he called this regularity the **law of octaves.** In 1865 he drew up a table in which the figures are **atomic numbers**, giving the serial order of the atomic weights beginning with hydrogen :

H	1	F	8	Cl	15	Co&Ni	22	Br	29	Pd	36	I	42	Pt&Ir	50
Li	2	Na	9	K	16	Cu	23	Rb	30	Ag	37	Cs	44	Tl	53
G	3	Mg	10	Ca	17	Zn	25	Sr	31	Cd	38	Ba&V	45	Pb	54
Bo	4	Al	11	Cr	19	Y	24	Ce&La	33	U	40	Ta	46	Th	56
C	5	Si	12	Ti	18	In	26	Zr	32	Sn	39	W	47	Hg	52
N	6	P	13	Mn	20	As	27	Di&Mo	34	Sb	41	Nb	48	Bi	55
O	7	S	14	Fe	21	Se	28	Ro&Ru	35	Te	43	Au	49	Os	51

Newlands inverted the order of some elements (*e.g.* Te and I), as was later done by Mendeléeff. He also pointed out that similar elements frequently appear in the same row, and suggested that all previous schemes of relations among atomic weights, " including the well-known triads, are merely arithmetical results flowing from the existence of the law of octaves ".

The order in Newlands's table was disturbed by some incorrect atomic weights (*e.g.* of uranium) and by the so-called transitional elements (Fe, Co, Ni ; platinum metals), but his idea contained the germ of the Periodic Law, afterwards stated by Mendeléeff in 1869 and by Lothar Meyer in 1870, neither of whom knew of the publications of De Chancourtois and Newlands. The " law of octaves " was

not well received, one facetious critic asking Newlands if he had ever tried arranging the elements in the order of the initial letters of their names!

The periodic law.—Mendeléeff's basic idea was that "there must be some bond of union between mass and the chemical elements; and as the mass of a substance is ultimately expressed in the atom, a functional dependence should exist and be discoverable between the individual properties of the elements and their atomic weights" (*Principles of Chemistry*, 1905, **2**, 30). His statement of the **periodic law** is given in eight paragraphs:

(1) The elements, if arranged according to their atomic weights, show an evident periodicity of properties.

(2) Elements which are similar as regards their chemical properties have atomic weights which are either of nearly the same value (platinum, iridium, osmium), or which increase regularly (potassium, rubidium, caesium).

(3) The arrangement of the elements, or of groups of elements, in the order of their atomic weights, corresponds with their so-called valencies.

(4) The elements which are most widely distributed in nature have small atomic weights, and . . . sharply defined properties. They are therefore typical elements.

(5) The magnitude of the atomic weight determines the character of an element.

(6) The discovery of many yet unknown elements may be expected.

(7) The atomic weight of an element may sometimes be corrected by the aid of a knowledge of those of adjacent elements.

(8) Certain characteristic properties of the elements can be foretold from their atomic weights.

The law may be stated in the form that *the properties of the elements are in periodic dependence on their atomic weights.* As the atomic weights increase steadily from 1 to 240, the elements divide into definite groups, so that sequences of similar elements recur in the same order.

The atomic volume curve.—The **atomic volume** of a *solid* element is the volume V c.c. of the atomic weight A in grams, *i.e.* the atomic weight divided by the density: $V = A/D$.

If the atoms in the solid are assumed to be spherical and in contact $\sqrt[3]{A/D}$ is a measure of the mean distance between the atomic centres. Mendeléeff remarked that reactive elements (alkali metals, halogens) have large atomic volumes, elements which are not very reactive (carbon as diamond, nickel, cobalt, iridium, and platinum) have small atomic volumes. Lothar Meyer in 1870 plotted atomic volumes against atomic weights, obtaining the **atomic volume curve.** In a modern form of this atomic numbers are used instead of atomic weights (cf. Hopkins, *J.A.C.S.*, 1911, **33**, 1005), which gives a more regular curve (Fig. 95).

The curve also shows a periodicity of other properties: expansion by heat, conductivity for heat and electricity, magnetic susceptibility, melting point, boiling point, refractive index, crystalline form, compressibility, hardness, malleability, volume change on fusion, atomic heats at low temperatures, frequency of atomic vibration in solids, electrode potentials of metals, over-

voltage of metals, heats of formation of oxides and chlorides, melting points of chlorides, viscosity and colour of salt solutions, mobilities of ions, valency, distribution of lines in spectra, and the distribution of the elements in nature.

Gaseous, and readily fusible, elements occur on the maxima and ascending parts of the curve ; difficultly fusible elements on the minima and descending parts. If the parts between two maxima are called a section, then elements on descending parts of the first two sections are electropositive (*i.e.* form basic oxides) and those on the ascending parts electronegative (*i.e.* form acidic oxides), except the inert gases. Elements on later sections have electrochemical properties passing through two periods whilst the atomic volume curve passes

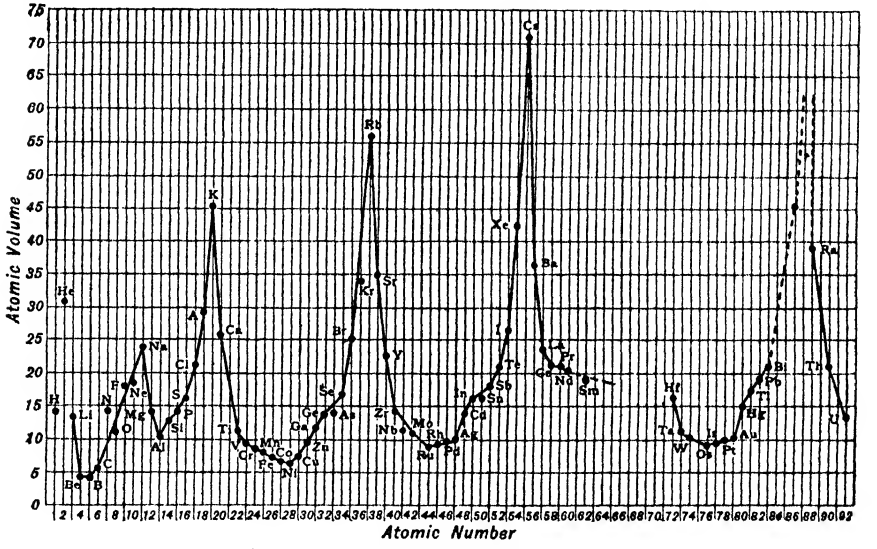


FIG. 95.—Atomic volume curve.

through one : strongly electropositive elements (K, Ca ; Rb, Sr ; Cs, Ba) occur on the first part of the descending curve, followed by more or less electronegative elements (V, Cr, Mn ; Zr, Nb, Mo, Ru, Rh), which are followed through the minima and on ascending parts by electropositive elements (Fe, Co, Ni, Cu, Zn, Ga ; Pd, Ag, Cd, In), and on higher parts of the ascending curve by electronegative elements (As, Se, Br ; Sn, Sb, Te, I).

The periodic table.—Mendeléeff and Lothar Meyer arranged the elements in different forms of a **periodic table** or **periodic system.** A modern form of Lothar Meyer's table is given here and one of Mendeléeff's on p. 182. In the table the elements are arranged in eight vertical **groups,** each divided into *a* and *b* **sub-groups.** These arise from suitably breaking up into horizontal **periods** the sequence of elements in the order of their atomic weights (with some exceptions noted below), the ordinal **atomic numbers** (not the atomic weights) being given in the table.

After the first three **short periods** containing 2, 8, and 8 elements, the **long periods** four, five and six contain 18, 18, and 32 elements, respectively (allowing for missing elements), and each long period is divided (in this form of the table) into two **series**, which are even or odd according to the number attached. Similar elements in the short periods recur in the same order, and elements in the vertical groups resemble one another closely (Li, Na ; Be, Mg ; etc.). In the long periods elements in the even *or* odd series only show close resemblances (K, Rb, Cs ; Ca, Sr, Ba, Ra ; etc., and Cu, Ag, Au ; Zn, Cd, Hg, etc.).

The atomic weights of argon and potassium are 40 and 39, which place them in the reverse order to the one shown, which puts them into groups in which the alkali metal sodium is associated with its chemical analogue potassium, and the inert gas neon with the inert gas argon. Four such pairs of **anomalous elements** occur in the table :

(1) A 40, K 39. (2) Co 59, Ni 58·7. (3) Te 128, I 127. (4) Th 232, Pa 230. This was formerly a puzzle, but its explanation became clear with the discovery of isotopes (p. 185).

SHORT PERIODIC TABLE

PERIOD.	SERIES.	GROUP. I. a	I. b	II. a	II. b	III. a	III. b	IV. a	IV. b	V. a	V. b	VI. a	VI. b	VII. a	VII. b	VIII. a	(o) b
1	1	H 1															He 2
2	2	Li 3		Be 4			B 5		C 6		N 7		O 8		F 9		Ne 10
3	3	Na 11		Mg 12			Al 13		Si 14		P 15		S 16		Cl 17		A 18
4	4	K 19		Ca 20			Sc 21		Ti 22		V 23		Cr 24		Mn 25	Fe 26 Co 27 Ni 28	
	5		Cu 29		Zn 30		Ga 31		Ge 32		As 33		Se 34		Br 35		Kr 36
5	6	Rb 37		Sr 38			Y 39		Zr 40		Nb 41		Mo 42		— 43	Ru 44 Rh 45 Pd 46	
	7		Ag 47		Cd 48		In 49		Sn 50		Sb 51		Te 52		I 53		Xe 54
6	8	Cs 55		Ba 56			15 Rare Earths 57–71		Hf 72		Ta 73		W 74		Re 75	Os 76 Ir 77 Pt 78	
	9		Au 79		Hg 80		Tl 81		Pb 82		Bi 83		Po 84		— 85		Em 86
7	10	— 87		Ra 88			Ac 89		Th 90		Pa 91		U 92				

The natural sequence runs along series 4 until manganese is reached. After this we should expect an inert gas like argon, but actually three elements are found, iron, cobalt and nickel, with atomic weights closer together than in the case of previous elements, and with very similar physical and chemical properties. All three are put in Group VIII*a* (no representatives of which occur in earlier periods) and were called by Mendeléeff **transitional elements**. The long

period of 18 elements then continues with the elements copper, zinc, etc., which do not closely resemble the preceding elements of their groups (potassium, calcium, etc.), and are therefore put in the *b* sub-groups or odd series. This long period is again closed by an inert gas, krypton. It is followed by a similar long period of 18 elements (No. 43, " masurium," being doubtful), again containing three transitional elements ruthenium, rhodium and palladium, and ending with an inert gas, xenon.

The next long period begins with the alkali metal caesium and proceeds normally as far as lanthanum in Group III. This is followed, however, not by a Group IV element like zirconium, but by a group of elements (one, No. 61, probably missing, since the existence of the element " illinium " has not been confirmed) with atomic weights differing by one, two, or even four units, all of which have very similar chemical properties and are difficult to separate. The 15 elements from lanthanum to lutecium are the elements of the **rare earths**, two of which (scandium and yttrium) occur in the earlier periods 4 and 5. The regular change in chemical character is thus checked after lanthanum, and goes on again only when the atomic weight has increased by 40 units. Then, after the last rare-earth element lutecium, the element hafnium (discovered by Coster and Hevesy in 1923) takes its place in Group IV under zirconium, to which it is very closely related. This place was formerly given to cerium, which must be put in Group III with the other rare-earth elements, the order of the rare-earth elements from atomic number 57 being : (i) lanthanum, cerium, praseodymium, neodymium, (illinium?), samarium and europium as the *cerite earth* elements, followed by (ii) gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutecium (No. 71) as the *gadolinite earth* elements. The placing of the rare earths is a difficulty in this " short " form of the table, but is more easily understood in the " long " form given later (p. 182).

After hafnium in Group IV, the elements follow normally to the three transitional elements osmium, iridium and platinum, after which the long period of 32 elements continues from gold (No. 85 in Group VII being missing) and is closed by the inert gaseous radioactive emanation. A new period, all the elements of which are strongly radioactive, begins with radium in Group II (No. 87 in Group I being missing) and continues as far as uranium in Group VI, when the period closes. We should expect many more elements in this period, by analogy with the numbers in the earlier periods, and the higher members may have disappeared because they were radioactive and have been transformed into elements of lower atomic weight. This, however, is only a surmise.

It may be noted that only elements taken from an odd *or* an even series obey the law of triads, *e.g.* Ca, Sr, Ba, *or* Zn, Cd, Hg in Group II. According to Paneth only elements in periods ending with an inert gas can form volatile hydrides (*e.g.* AsH_3, SbH_3, SnH_4, BiH_3), the others forming salt-like hydrides (*e.g.* LiH, NaH, KH, BaH_2).

The periodicity of valency.—Mendeléeff pointed out that the number of a group corresponds with the **valency** of the elements in it. The valency is a

measure of the *combining capacity* of an element and is *equal to the number of atoms of hydrogen* (or of chlorine or fluorine, or twice the number of atoms of oxygen) *combining with or displaced by one atom of the element* (*College Course*, Chap. X). In some cases (P, S, Cl, Cr, Mn) the maximum valency, in others (Cu, Ag, Au) the minimum, is equal to the period number, and the assignment seems rather artificial, as Wyruboff (1896) said; the reason is now fairly clear from the point of view of atomic structure (p. 264). The full sequence of valencies is seen with the fluorine and oxygen compounds:

I	II	III	IV	V	VI	VII	VIII
LiF	BeF_2	BF_3	CF_4	PF_5	SF_6	IF_7	OsF_8
Cs_2O	BaO	Al_2O_3	SnO_2	Ta_2O_5	WO_3	Mn_2O_7	OsO_4

whilst the hydrogen valency increases from 1 to 4 and then decreases again to 1:

$$LiH \quad CaH_2 \quad LaH_3 \quad CH_4 \quad NH_3 \quad SH_2 \quad ClH.$$

The zero-valent inert gases of Group VIII*b* (or Group 0, as it is sometimes called) separate the strongly electronegative elements of Group VII from the strongly electropositive elements of Group I; the transitional elements of Group VIII*a* do this for the three parts of long periods where there is no inert gas, but in this case the positive and negative properties of the Group I and Group VII elements are less marked:

$$\overset{-}{F}Ne\overset{+}{Na} \qquad \overset{-}{Cl}A\overset{+}{K} \qquad \overset{-}{Br}Kr\overset{+}{Rb} \qquad \overset{-}{I}Xe\overset{+}{Cs}$$

$$\overset{-}{Mn}(Fe, Co, Ni)\overset{+}{Cu} \qquad \overset{-}{Ma}(?)\ (Ru, Rh, Pd)\ \overset{+}{Ag} \qquad \overset{-}{Re}\ (Os, Ir, Pt)\ \overset{+}{Au}$$

Abegg (*Z. anorg. Chem.*, 1904, **39**, 330) distinguished the polar character of an element by: (1) ionisation, *e.g.* $HCl = H^+ + Cl^-$; (2) hydrolysis, *e.g.* $P_3N_5 + 12H_2O = 3H_3\overset{-}{P}\overset{+}{O}_4 + 5\overset{-}{N}H_3\overset{+}{}$; (3) position in the periodic system as compared with that of other elements with which it combines, *e.g.* $\overset{+}{S}_2\overset{-}{Cl}_2$; (4) the formulae of compounds in which it exerts its maximum valency. The last criterion is based on Abegg's theory that an element has a **normal valency** and a **contravalency**, the sum of which is equal to eight, *e.g.* S in H_2S^{-2} and $S^{6+}O_3$:

Group	-	I	II	III	IV	V	VI	VII
Normal valency	-	+1	+2	+3	±4	−3	−2	−1
Contravalency	-	(−7)	(−6)	(−5)		+5	+6	+7

The non-metallic elements are found only in the upper right-hand part of the table. The change of electrochemical character is seen in the basic (+), acidic (−), and amphoteric (±) character of the oxides:

$$\underset{+}{Na_2O} \quad \underset{+}{MgO} \quad \underset{\pm}{Al_2O_3} \quad \underset{-}{SiO_2} \quad \underset{-}{P_2O_5} \quad \underset{-}{SO_3} \quad \underset{-}{Cl_2O_7}$$

(An amphoteric oxide is one which behaves as a weakly basic oxide towards strong acids and a weakly acidic oxide towards strong bases.)

The last members of the even series may resemble the first members of the next odd series (excluding the inert gases), *e.g* there is a gradual transition from chromium and manganese to copper and zinc. Since the electropositive

character decreases from left to right in a period, but usually increases in passing down a group, there are some striking resemblances between pairs of elements in diagonal positions in the first two periods, *e.g.* Li and Mg, Be and Al, B and Si.

There are interesting regularities in the numbers of elements in the periods. Rydberg (1914) pointed out that the numbers 2, 8, 18 and 32 can be written $2 \cdot 1^2$, $2 \cdot 2^2$, $2 \cdot 3^2$ and $2 \cdot 4^2$, and Bohr (1921) that they can also be written 1·2, 2·4, 3·6 and 4·8. Rydberg thought two gases should come between hydrogen and helium, which he identified with the " coronium " and " nebulium " supposed to correspond with lines in the spectra of the sun, some nebulae, and possibly volcanic gases, but these spectra are now known to be due to common elements such as oxygen.

The gaseous hydrides.—An examination of the Periodic Table (Paneth, *Ber.*, 1920, **53**, 1710; 1925, **58**, 1138) shows that all elements occupying places 1 to 4 before an inert gas (and also boron) can form gaseous hydrides. Elements in Groups I–III*a* (except boron) give salt-like solid hydrides, such as NaH. Beryllium and magnesium resemble zinc in not forming hydrides. The volatile hydrides are covalent compounds, whilst the solid hydrides are conducting when fused, the hydrogen behaving as an anion (Li^+H^-). A different group of hydrides comprises the metallic hydrides CuH, Pd_2H and NiH_2. Silver hydride, however, is said to be salt-like and to be produced by the prolonged action of atomic hydrogen on silver foil.

I	II	III	IV	V	VI	VII	VIII*a*
Li	—	B	C	N	O	F	Ne
Na	—		Si	P	S	Cl	A
K	Ca		Ge	As	Se	Br	Kr
Rb	Sr		Sn	Sb	Te	I	Xe
Cs	Ba	La	Pb	Bi	Po	—	Em
		etc.					

Correction of atomic weights.—Mendeléeff, by fixing the positions of the elements in the periodic table, was able to correct some atomic weights in use in 1869, whilst Lothar Meyer thought " it would be rash to change the accepted atomic weights on the basis of so uncertain a starting point ". Mendeléeff's changes have mostly been confirmed.

(i) From its occurrence with zinc, **indium** was supposed to be bivalent and its atomic weight $2 \times 38 = 76$. There is no room in Group II for an element of atomic weight 76, the place after zinc (65) being occupied by strontium (87). There is also no vacant place between As (75) and Se (79) Mendeléeff pointed out that if indium is tervalent with atomic weight $3 \times 38 = 114$ it would fill a space then vacant in Group III between cadmium (112) in Group II and tin (118) in Group IV, and the physical and chemical properties of indium agree with this. The densities are Cd 8·6, In 7·4, Sn 7·2; the basicity of In_2O_3 is intermediate between those of CdO and SnO_2. This position was confirmed by the specific heat 0·055, giving an atomic weight $6 \cdot 3/0 \cdot 055 = 114 \cdot 5$, and the discovery of indium alums, in which indium is tervalent.

(ii) From its resemblance to aluminium, **beryllium** was considered to be tervalent. The hydroxides of beryllium and aluminium are gelatinous precipitates soluble in acids and alkalis; the normal carbonates cannot be prepared by precipitation, as they hydrolyse; and the metals, obtained by electrolysis of the fused double potassium fluorides, dissolve in alkalis with liberation of hydrogen. The specific heat of beryllium gave 14·8 for the atomic weight. But there is no place for an element of atomic weight $3 \times 4{\cdot}5 = 13{\cdot}5$ in the first period. Avdéeff (1819) had previously pointed out the analogy between magnesium and beryllium, and Mendeléeff assumed beryllium to be bivalent and placed it in Group II before magnesium, where there is a vacant space for an element of atomic weight $2 \times 4{\cdot}5 = 9$ between Li (7) and B (11). Humpidge (1885–6) then found that the specific heat of beryllium increases rapidly with temperature and at 500° is 0·6206, giving an atomic weight 9·8, and Nilson and Pettersson (1884), who had previously regarded beryllium as tervalent, found the value 40 for the vapour density (H = 1) of beryllium chloride, which agrees with $BeCl_2$ $(9 + 71 = 80)$ but not with $BeCl_3$ $(13{\cdot}5 + 106{\cdot}5 = 120)$.

(iii) **Uranium** was regarded as tervalent with an atomic weight of $3 \times 40 = 120$. Mendeléeff pointed out that there was no place in Group III for such an element and, emphasising its resemblance to chromium, molybdenum and tungsten, he doubled the atomic weight, placing uranium below tungsten in Group VI. The oxides were formulated as UO_2, U_3O_8 and UO_3. Zimmermann in 1880 showed that the vapour density of a volatile chloride of uranium corresponds with an approximate molecular weight of 382. Since the chloride contained 37·34 p.c. of chlorine, the molecular weight contains 142·5 parts of chlorine, or approximately $4 \times 35{\cdot}5 = 142$ parts, so that the formula of the chloride is U_xCl_4. The specific heat of uranium is 0·0276, hence the atomic weight is approximately $6{\cdot}3/0{\cdot}0276 = 228$. But $382 - 142 = 240$, which is sufficiently near 228 to show that $x = 1$ and the atomic weight of uranium is $6 \times 40 = 240$.

Prediction of missing elements.—Mendeléeff found that when the known elements are assigned to their groups in the periodic table, gaps must be left for unknown elements, and from the properties of adjacent elements he was able to predict the properties of these unknown elements, which were found to agree closely with the observed properties when they were afterwards discovered. The next element known after calcium (Ca = 40) was titanium (Ti = 48), which obviously belongs to Group IV, leaving a vacant space below aluminium in Group III. Two similar gaps were found in the next period:

Be 9	B 11	C 12	N 14
Mg 24	Al 27	Si 28	P 31
Ca 40	—	Ti 48	V 51
Zn 65	—	—	As 75

Mendeléeff predicted that these vacant spaces would be filled by elements which he called *eka-boron*, *eka-aluminium* and *eka-silicon* (Sanskrit *eka* = one), respectively, and in 1871 he predicted their properties. These predictions were brilliantly verified by the discovery of **scandium** (Nilson, 1879), **gallium** (Lecoq de Boisbaudran, 1875) and **germanium** (Winkler, 1886), respectively. The table below gives the predicted and observed properties of eka-silicon or germanium (Mendeléeff, *Principles of Chemistry*, 1906, **2**, 27):

Eka-Silicon, Es	Germanium, Ge
Atomic weight, 72.	Atomic weight, 72·6.
Density, 5·5.	Density, 5·47.
Atomic volume, 13.	Atomic volume, 13·2.
Colour dirty grey, giving a white powder of EsO_2.	Colour greyish-white, giving a white powder of GeO_2.
Metal will decompose steam with difficulty.	Metal does not decompose water.
Action of acids slight, of alkalis more pronounced.	Metal not attacked by HCl, dissolves in aqua regia; aqueous KOH has no action, but fused KOH oxidises with incandescence.
Element obtained by reduction of EsO_2 or K_2EsF_6 by Na.	Element obtained by reduction of GeO_2 by C or of K_2GeF_6 by Na.
Oxide EsO_2 refractory, s.g. 4·7; less basic than TiO_2 or SnO_2, but more basic than SiO_2.	Oxide GeO_2 refractory, s.g. 4·703; very feebly basic, forms germanates.
Hydroxide soluble in acids, but solutions readily precipitate metahydroxide by hydrolysis.	Acids do not pp. hydroxide from dil. alkaline solutions, but from conc. solutions acids or CO_2 ppt. GeO_2 or metahydroxide.
Chloride $EsCl_4$ liquid, b.p. below 100°, s.g. 1·9 at 0°.	Chloride $GeCl_4$ liquid, b.p. 86·5°, s.g. 1·887 at 18°.
Fluoride EsF_4 not gaseous.	Fluoride $GeF_4,3H_2O$, a white crystalline solid.
Organo-metallic compounds formed, *e.g.* $Es(C_2H_5)_4$, b.p. 160°, s.g. 0·96.	$Ge(C_2H_5)_4$, b.p. 160°, s.g. slightly less than 1·0.

When Ramsay discovered the inert gases helium and argon he recognised that they must belong to a new group of zero-valent elements, and that there must be other elements in this group. These were sought and found; neon, krypton and xenon by Ramsay and Travers, and radium emanation by Ramsay.

The gaps for elements 43, 75, 84, 85 and 87 have always been recognised, and (when the exact number of rare-earth elements became known) 61 and 72 were added. Of these, 72, 75 and 84 have been filled by hafnium, rhenium and polonium, respectively; 43 was supposed to be filled by masurium and 61 by illinium, but these elements are now regarded as doubtful, and although eka-iodine 85 and eka-caesium 87 have been more than once reported, the discoveries have not been substantiated. (Radioactive isotopes of some of these missing elements have been artificially obtained; see p. 205.)

Difficulties in the periodic table.—Some features of the periodic table were difficult to explain, although most of them have since been cleared up by increasing knowledge of the structure of the atom.

(1) The **inverted positions** of the pairs of elements A, K; Co, Ni; Te, I; Th, Pa. This is caused by the occurrence of isotopes (p. 185).

(2) The difficulty of fitting in the **rare-earth elements**. This is explained by their atomic structure, which shows that the valency and chemical properties remain constant over a large increase of atomic number (p. 435).

(3) The **transitional elements** seemed to occupy an anomalous position and attempts to include them in other groups were unsuccessful. The theory of atomic structure again shows that the three sets of transitional elements take their place along with other elements now regarded as transitional elements in the wider sense (p. 261)

(4) Some **chemical analogies** are overlooked, *e.g.* those between boron and silicon, and copper and mercury, whilst some elements with little analogy, such as copper and the alkali metals, and manganese and the halogens, are brought together The analogies between successive elements in a *period*, pointed out by Mendeléeff, has, however, sometimes been overlooked. Thus, the metals of

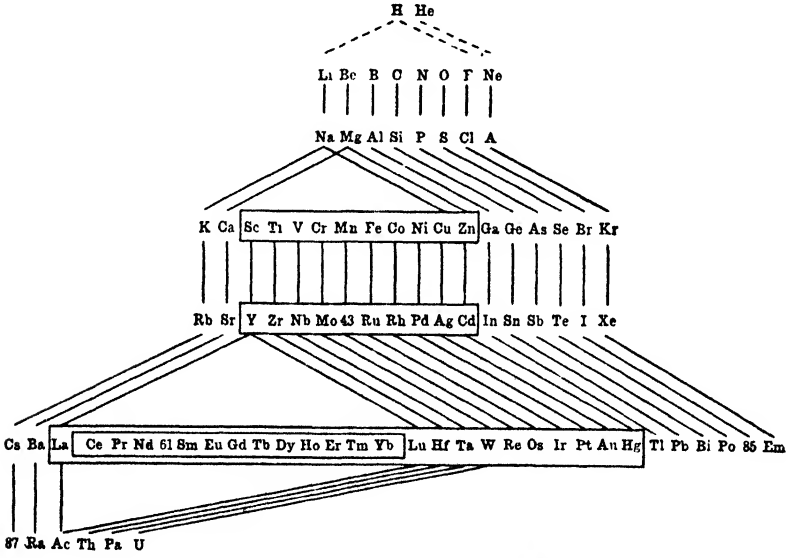


FIG. 96.—Long Periodic Table.

the horizontal period V, Cr, Mn, Fe, Co, Ni, Cu and Zn (transitional elements in the wider sense) are chemically related and their sulphates $M^{II}SO_4, 7H_2O$ are isomorphous. It must be admitted, however, that some older classifications bring some very similar elements together which are separated in the periodic table.

(5) The **position of hydrogen**, which shares a whole period with helium, seems anomalous. If placed in Group I on account of its resemblance to the alkali metals in valency, in electropositive character, and in forming an alloy with palladium, there seem to be gaps in the period in Groups II to VII, and there can only be a change in atomic weight from 1 to 4, which would not accommodate so many elements. If placed in Group VII because it is a non-metal, can be replaced by halogens in organic compounds, forms salt-like hydrides such as NaH (similar to NaCl), and is a gas more difficult to liquefy than

slit, the ions are then bent by a magnetic field into a semicircular path, so that they are just able to pass through a second slit into an electroscope. With a

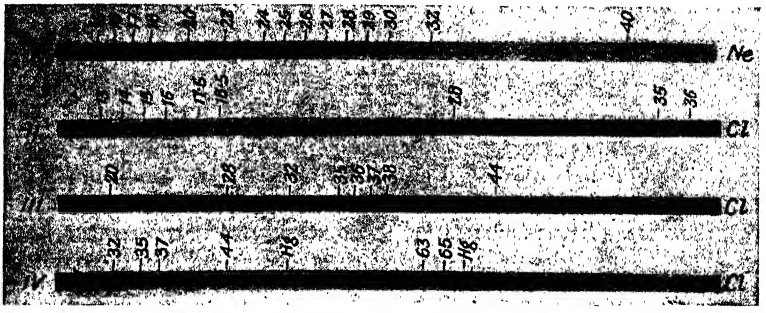


FIG. 100.—Mass spectra (Aston, 1921).
The lines additional to those of the isotopes of the elements indicated are due to impurities in the discharge tube.

constant magnetic field, the potential difference required to cause the ions to pass through the fixed second slit is inversely proportional to m/e for the ion, the value of which is so determined. This method has been improved by Bainbridge (1932), whose apparatus has been much used in recent work.

A sensitive method for the detection of isotopes depends on **spectroscopic measurements.** In the case of hydrogen and deuterium, when the atomic masses are widely different, the *atomic line spectrum* enables the isotopes to be distinguished (p. 256), but in all other cases the *molecular band spectra* are used. These are of three main types :

(1) Absorption spectra in the far infra-red due to changes in the rotational energy of the molecule. These were used to detect the isotopes ^{35}Cl and ^{37}Cl in gaseous hydrogen chloride.

(2) Absorption spectra in the near infra-red due to simultaneous changes in rotational and vibrational energy. These confirmed the isotopic effect in HCl.

(3) Band spectra in the visible or ultra-violet regions due to electronic transitions combined with changes in vibrational and rotational energy, and (unlike (1) and (2)) given by non-polar as well as polar molecules. They led to the detection of isotopes of oxygen (^{17}O, ^{18}O), nitrogen (^{15}N) and carbon (^{13}C).

If the force-fields in the isotopic molecules $^{p}X^{a}Y$ and $^{p}X^{b}Y$ are identical, where a and b are the isotopic masses, the rotational energies are inversely as the moments of inertia for corresponding states, and the vibrational energies are inversely as the square roots of the reduced masses :

$$\rho_a = ap/(a+p) \quad \text{and} \quad \rho_b = bp/(b+p).$$

Hence, apart from a small correction (Watson, *Phys. Rev.*, 1934, **46**, 319 ; 1936, **49**, 70), the rotational frequencies are in the ratio of the values of $1/\rho$ and the vibrational frequencies in the ratio of $1/\sqrt{\rho}$. Hence ρ may be calculated from the displacements of corresponding lines in the band spectrum, and thus a and b calculated.

Occurrence of isotopes.—The proportion of the isotopes in an isotopic mixture is very variable with different elements. Some isotopes occur only in very minute amounts. The relative abundance of ^{16}O and ^{124}Xe has been given as $10^{17} : 1$. In hydrogen, the atomic ratio is $^{1}H : {}^{2}H = 6900 : 1$; bromine is a mixture of approximately equal parts of ^{79}Br and ^{81}Br. Apart from the well-known case of the isotopes of lead produced by the radioactive changes of uranium (^{206}Pb) and thorium (^{208}Pb), slight differences in the atomic weights of different specimens of some natural elements have been found. Atmospheric oxygen is slightly richer in ^{18}O than water oxygen, and small differences in the density of water from different sources are reported. There are also small variations in the carbon ^{12}C and ^{13}C isotope ratio (90 : 1) in various natural materials (Nier and Gulbransen, *J.A.C.S.*, 1939, **61**, 698). All these differences are very slight.

Separation of isotopes.—The *artificial separation of isotopes* has been achieved by several methods (cf. Champetier, *Bull. Soc. Chim.*, 1936, **3**, 1701; *Nature*, 1937, **139**, 38).

(1) Minute amounts of the lithium isotopes, and more appreciable amounts of the potassium isotopes, have been separated by the *mass spectrograph*, the different rays being collected on appropriate targets.

(2) Mercury, zinc, potassium and chlorine (in hydrogen chloride) isotopes have been separated by *distillation at very low pressures*. The apparatus used by Brönsted and Hevesy (1921) for mercury consisted of a spherical vessel containing mercury at 40°–60°, the vapour being condensed on a spherical concentric bulb cooled with liquid air inside it. Since the pressure was very low the distance (1–2 cm.) between the mercury surface and condenser was of the order of the mean free path of the mercury molecules, and as there was no return of evaporated molecules to the liquid surface, the relative rates of distillation depended only on the molecular velocities, *i.e.* on the masses of the molecules. The residual mercury contained the heavier isotopes, the condensed mercury the lighter, and the densities were found to be 1·00023 and 0·99974 when normal mercury is 1. The atomic weights confirmed the separation.

(3) *Fractional distillation* has been used with neon, hydrogen, water, ammonia, oxygen and carbon tetrachloride.

(4) The *diffusion method* gives better results. If x_0 and y_0 are the volumes of the two constituents in the original gaseous mixture, and x and y the volumes remaining after diffusion, the enrichment coefficient $r = (y/y_0) \div (x/x_0)$ is related to the isotopic masses m_1 and m_2 by the equation $r = a\sqrt{V_0/V}$, where

$$a = (m_1 + m_2)/(m_1 - m_2); \quad V_0 = x_0 + y_0; \quad V = x + y.$$

The value of a for HD (D = ^{2}H) and H_2 is 5, for neon 21, and for $^{18}O^{16}O$ and $^{16}O^{16}O$, 33. The diffusion method has been used with batteries of porous clay tubes in series, and also by diffusion into the mercury vapour of the pumps circulating the gas. By the first method, pure ^{20}Ne has been obtained, and in 8 hours 1 c.c. of pure D_2 from a mixture containing only 1 in 1000 of D_2. A partial separation of the carbon isotopes ^{12}C and ^{13}C has been achieved by diffusion of methane. Diffusion of hydrogen and deuterium through heated palladium has also been used.

(5) The *electrolytic method* is most successfully used in the separation of hydrogen and deuterium from water. A slight separation of the oxygen isotopes is also effected, but it has been calculated that, to obtain 1 c.c. of $H_2{}^{18}O$ by this process, it would be necessary to electrolyse more water than is found on the surface of the earth.

(6) Some separation of isotopes has been achieved by chemical means, generally by so-called *exchange reactions*, of which the following are typical:

$$NH_3 + HOD \rightleftharpoons NH_2D + H_2O$$
$$2H_2{}^{18}O + C^{16}O_2 \rightleftharpoons 2H_2{}^{16}O + C^{18}O_2.$$

(7) The *photochemical method* is probably capable of extension. Phosgene $COCl_2$ containing the chlorine isotopes 35 and 37 is exposed to light, when the molecules containing ^{35}Cl are preferentially decomposed (in presence of a trace of iodine). The free chlorine is absorbed by mercury and has an atomic weight lower than normal.

(8) The *thermal diffusion method* (Clusius and Dickel, 1938) uses a long vertical tube containing the gas with an axial wire, electrically heated to 500° or more. The heavier molecules accumulate in the cooler region. The gas rises to the top, flows down the cold wall and again rises in the central part. This " thermal siphoning " combines with the thermal diffusion from the hot wire, and as a result the heavier molecules accumulate at the bottom of the tube and the lighter at the top. A very effective separation can be achieved (*Ann. Rep. C.S.*, 1940, 155).

Table of Isotopes

The isotopic masses *A rounded off to whole numbers* of natural elements of atomic number $Z = 0$ (the neutron: see p. 201) to 92 are given. The order is that of masses, not of abundance of occurrence. Radioactive species are starred.

Z		A
0	*n*	1
1	H	1, 2
2	He	3, 4
3	Li	6, 7
4	Be	9
5	B	10, 11
6	C	12, 13
7	N	14, 15
8	O	16, 17, 18
9	F	19
10	Ne	20, 21, 22
11	Na	23
12	Mg	24, 25, 26
13	Al	27
14	Si	28, 29, 30
15	P	31
16	S	32, 33, 34, 36
17	Cl	35, 37
18	A	36, 38, 40
19	K	39, *40, 41
20	Ca	40, 42, 43, 44, 46, 48
21	Sc	45
22	Ti	46, 47, 48, 49, 50
23	V	51
24	Cr	50, 52, 53, 54
25	Mn	55
26	Fe	54, 56, 57, 58
27	Co	57, 59
28	Ni	58, 60, 61, 62, 64
29	Cu	63, 65
30	Zn	64, 66, 67, 68, 70
31	Ga	69, 71
32	Ge	70, 72, 73, 74, 76
33	As	75
34	Se	74, 76, 77, 78, 80, 82
35	Br	79, 81
36	Kr	78, 80, 82, 83, 84, 86
37	Rb	85, *87
38	Sr	84, 86, 87, 88
39	Y	89
40	Zr	90, 91, 92, 94, 96
41	Nb	93
42	Mo	92, 94, 95, 96, 97, 98, 100
44	Ru	96, 98, 99, 100, 101, 102, 104
45	Rh	101, 103
46	Pd	102, 104, 105, 106, 108, 110
47	Ag	107, 109
48	Cd	106, 108, 110, 111, 112, 113, 114, 116
49	In	113, 115

Z		A
50	Sn	112, 114, 115, 116, 117, 118, 119, 120, 122, 124
51	Sb	121, 123
52	Te	120, 122, 123, 124, 125, 126, 128, 130
53	I	127
54	Xe	124, 126, 128, 129, 130, 131, 132, 134, 136
55	Cs	133
56	Ba	130, 132, 134, 135, 136, 137, 138
57	La	139
58	Ce	136, 138, 140, 142
59	Pr	141
60	Nd	142, 143, 144, 145, 146, 148, 150
62	Sm	144, 147, *148, 149, 150, 152, 154
63	Eu	151, 153
64	Gd	152, 154, 155, 156, 157, 158, 160
65	Tb	159
66	Dy	158, 160, 161, 162, 163, 164
67	Ho	165
68	Er	162, 164, 166, 167, 168, 170
69	Tm	169
70	Yb	168, 170, 171, 172, 173, 174, 176
71	Lu	175, *176
72	Hf	172?, 174, 176, 177, 178, 179, 180
73	Ta	181
74	W	180, 182, 183, 184, 186
75	Re	185, 187
76	Os	184, 186, 187, 188, 189, 190, 192
77	Ir	191, 193
78	Pt	192, 194, 195, 196, 198
79	Au	197
80	Hg	196, 198, 199, 200, 201, 202, 204
81	Tl	203, 205
82	Pb	204, 206, 207, 208
83	Bi	209
90	Th	*232
91	Pa	*231
92	U	*234, *235, *238

It will be noticed in the table that :

(i) Several isotopes of different elements have the same mass (*e.g.* A, K, 40 ; Ni, Zn, 64 ; Kr, Sr, 86) ; these are called *isobars*.

(ii) Elements of *odd* atomic number are either simple or (except potassium) have only two isotopes, and for elements heavier than phosphorus (except potassium, lutecium and actinium) the isotopes have odd mass numbers (*A*) mostly differing by two units. Elements of *even* atomic number (greater than 6) have several isotopes.

Aston called the difference between the isotopic mass and the nearest whole number, divided by the isotopic mass, the **packing fraction**. It represents approximately the average gain or loss in mass per proton in the atom as compared with the state of nuclear packing in oxygen. Thus, the mass of ^{58}Ni is 57·942, hence the packing fraction is $-0{\cdot}058/58 = -10 \times 10^{-4}$.

The table does not include the large number of unstable radioactive isotopes produced artificially by nuclear bombardment (p. 205). These may have mass numbers outside the range of mass numbers of stable isotopes at both ends (*e.g.* ^{34}Cl, ^{38}Cl), and also missing intermediate mass numbers (*e.g.* ^{64}Cu, ^{80}Br).

It should be noted that the atomic masses with reference to $^{16}O = 16$ (the oxygen isotope of mass 16) are not really the whole numbers given in the table ; some accurate values (the figures in the third column are from earlier determinations) are :

^{1}H	1·00813	^{19}F	19·0045	^{31}P	30·983
^{2}H(D)	2·01473	^{20}Ne	19·9983	^{35}Cl	34·983
^{4}He	4·00389	^{27}Al	26·9909	^{37}Cl	36·980
^{10}B	10·0161	^{28}Si	27·9868	^{64}Zn	63·937
^{12}C	12·00386	^{29}Si	28·9866	^{79}Br	78·929
^{14}N	14·0075	^{40}A	39·9750	^{200}Hg	200·016

The mass spectrograph atomic masses (referred to the oxygen isotope $^{16}O = 16$) are converted to the chemical atomic weights (referred to the isotopic mixture $O = 16$) by division by 1·000275.

Some exact values of the masses have been found from the results of disintegration experiments (p 208).

Atomic Numbers

X-rays.—When cathode rays strike a material target, which in the X-ray tube consists of a metal (*e.g.* tungsten) plate called an *anti-cathode*, this emits a radiation which passes outside the tube and is capable of penetrating freely through paper, wood, aluminium and flesh, but is more or less absorbed by lead, platinum, glass or bone. These so-called **X-rays** were discovered by Röntgen in 1895; they have been produced sufficiently penetrating to pass through two inches of steel. They (1) affect a photographic plate, (2) cause fluorescence when they fall on substances such as barium platinocyanide, and (3) render a gas conducting or produce *ionisation* in it, charged particles being formed, and hence a gold-leaf electroscope loses its charge when exposed to X-rays, the surrounding ionised air conducting away the charge.

The X-rays are *electromagnetic waves* similar to light but of much smaller wave-length (below 500 A.; the lower limit of the visible spectrum is about 4000 A.; 1 Ångström unit (A.) is 10^{-8} cm. or 10^{-10} m.). This was proved by Friedrich, Knipping and Laue in 1912 by diffraction of X-rays passing through a crystal (p. 238).

Atomic numbers.—Barkla, and Kaye, in 1909 found that a solid element when bombarded by a sufficiently fast stream of cathode rays emits a characteristic X-radiation. This may be resolved into a spectrum by reflexion from a crystal (acting as a diffraction grating). Moseley, working at Oxford and Manchester in 1913–14, used a crystal of potassium ferrocyanide, and photographed the X-ray spectra of various elements (*Phil. Mag.*, 1913, **26**, 102; 1914, **27**, 703).

The elements (*e.g.* W, Fe, Cu) or their solid compounds (*e.g.* KCl) were used as anticathodes, being mounted on a trolley in an X-ray bulb so that they could be brought in succession in front of the cathode. Several kinds of rays, the *K*, *L*, *M*, *N* and *O*, have been detected, the first two by Moseley and the others by later workers. The *K*-radiations are of the shortest wave-length and are emitted by elements of small atomic weight to those of highest. The *L*-radiation of elements is shown from copper and elements of higher atomic weight, and is of longer wave-length than the *K*-radiation, and the *M*, *N*, and *O*-radiations, shown by heavier elements, are of still longer wave-lengths. The *K*-radiation of each element consists of four lines, but these appear as two pairs in each of which the two lines are very close together and were not resolved in Moseley's photographs. The *L*-radiation gives a larger number of lines than the *K*; in the case of tungsten, Siegbahn measured eighteen lines in the *L* spectrum.

The *K* spectra obtained by Moseley consisted in all cases of two lines K_α and K_β (really the two *K* pairs), one stronger than the other, the wave-

lengths of which decreased in a regular manner as the atomic weights of the elements increased. In Fig. 101, given by Moseley, the spectra are placed approximately in register, parts representing the same angle of reflexion by the crystal being in the same vertical line.

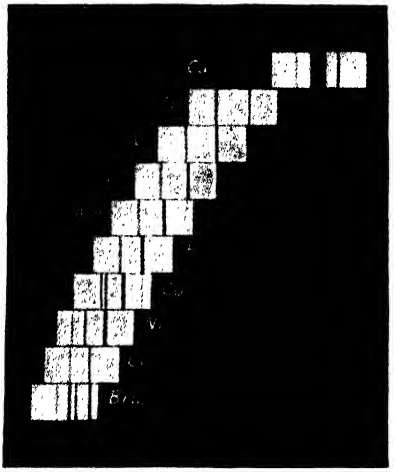


FIG. 101. X-ray spectra (Moseley). *K*-rays.

The elements, beginning with Ca at the top, are in the order of their occurrence in the Periodic Table (p. 176), with the ordinal numbers (*atomic numbers*, p. 175) running from Ca 20 to Zn 30, the element Sc (No. 21) being missing. The Zn lines, with those of Cu, are shown by brass. The Co spectrum shows a faint Ni line due to impurity. The gap where Sc should come is clearly seen, since the Ca lines are shifted much more to the right in comparison with those of Ti than in any other pair in the diagram. It is seen that with increasing atomic number the wave-length becomes increasingly smaller.

The wave-lengths λ of the emitted X-rays can be found from the angles of reflexion (p. 238). The frequencies n are given by $\mathbf{c} = n\lambda$, where $\mathbf{c}$ is the velocity of light. Generally, the *wave-number* $\nu = 1/\lambda$ is used instead of the frequency.

The square-roots of the wave-numbers of corresponding strong K_α lines in the spectra of successive elements taken in the order of their *atomic numbers* give practically a straight line. In Fig. 102, the square roots of the frequencies of the *K*, *L*, *M*, and *N* series are plotted against the atomic numbers of the elements. If ν is the wave-number of the K_α line, ν_0 a constant (Rydberg's constant), and N the atomic number, then Moseley found that :

$$Q = \sqrt{\nu/\tfrac{3}{4}\nu_0} = N - 1.$$

Element - -	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Atomic weight -	40	—	48	51	52	55	56	59	58·5	63	65
Q - - -	19	—	21	22	23	24	25	26	27	28	29
N - - -	20	21	22	23	24	25	26	27	28	29	30

Moseley's law shows that the order of values of Q is the same as that of the elements in the periodic table, although in some cases (*e.g.* Co and Ni ; Te, I) the order of atomic weights is reversed. The atomic numbers of Cl and K, deduced from the equation, are 17 and 19, leaving a gap, 18, for argon, although the latter has an atomic weight higher than that of potassium. Moseley's law gives the places in the sequence of atomic numbers where there are missing elements. In this way the elements of number 43, 61, 72, 75, 85 and 87 were found to be missing, and some of these were afterwards discovered.

The **atomic number** of an element is primarily the ordinal number of its position in the periodic table (p. 175), which was fixed by the chemical pro-

perties long before Moseley's researches, but these showed that the atomic number could be determined independently of the chemical properties from the X-ray spectra through the relation $Q = N - 1$. The Q values showed that there was one rare-earth element (No. 61) missing between lanthanum and

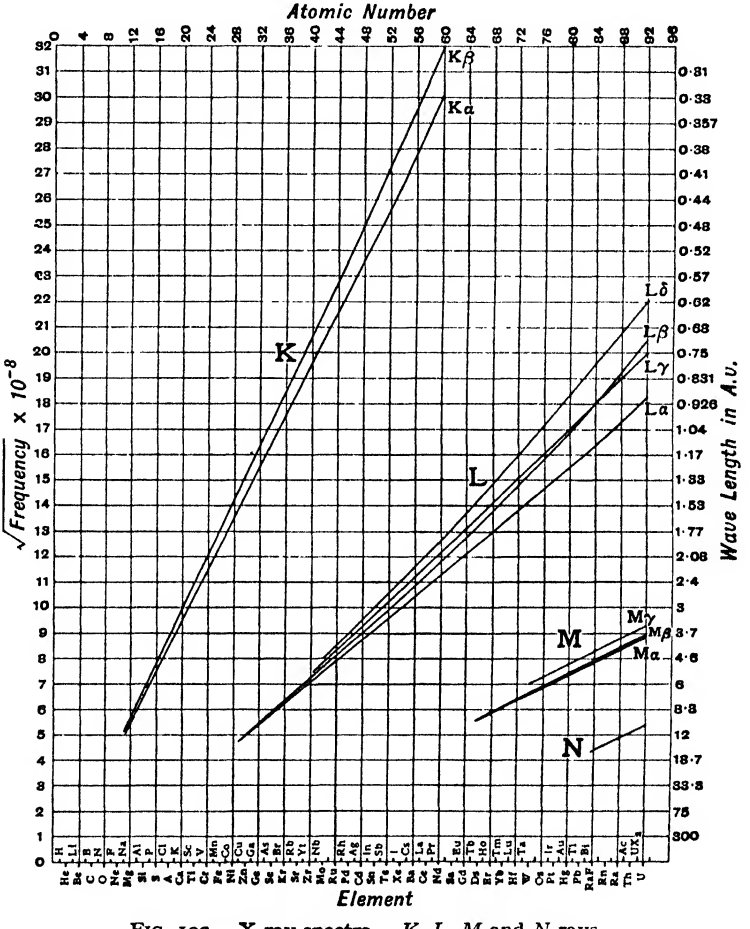


FIG. 102.—X-ray spectra. *K*, *L*, *M* and *N* rays.

lutecium and also that element No. 72 after lutecium was missing. Moseley's method did not show whether No. 72 was a rare-earth element or not; at first it was considered to be a rare-earth element, but the predictions of Bohr and the discovery of hafnium showed on *chemical* grounds that it was not, but belongs to Group IV.

Refinements in X-ray spectroscopy show that the linear character of the *L*, *M*, *N* and *O* series is only approximate, and that the curves show definite

changes of direction. The ordinates in Fig. 103 are $\sqrt{\nu/\nu_0}$, where ν_0 is Rydberg's constant, plotted against the atomic numbers. The breaks are important in the theory of atomic structure, since they occur at the beginning and end of successions of elements closely related in chemical properties, *e.g.* scandium to zinc, yttrium to cadmium, etc. In these the transition from one element to the

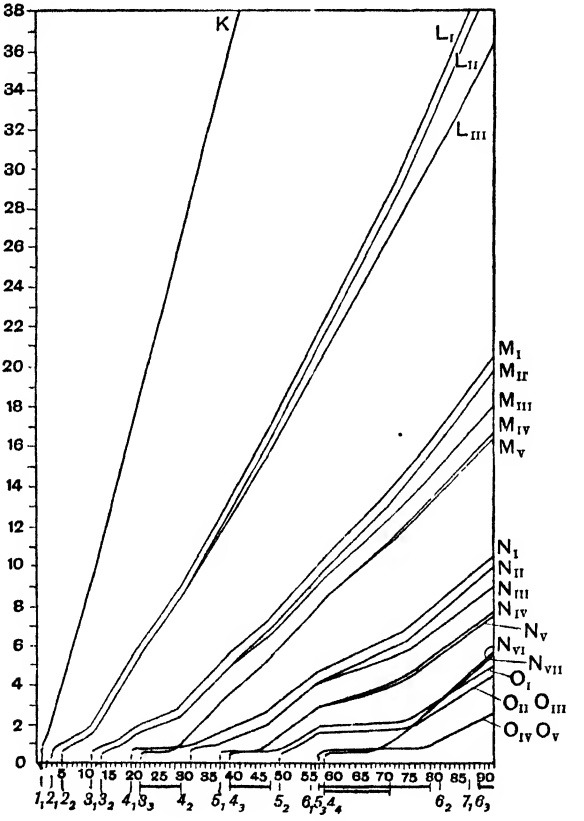


FIG. 103.—X-ray spectra.

K, L, M, N and *O* rays, due to groups of electrons having quantum numbers given (in Bohr's notation) in the last line (see p. 257).

next, instead of leading to a marked change of properties as usual, produces little change, and since the relation to the transitional elements of Group VIII is apparent, these sequences of elements are also called " transitional series " in the wider sense. They are shown in frames in Bohr's table (p. 182). This preservation of essential chemical properties is most apparent in the group of the rare-earth elements (Nos. 57–71). An explanation of this behaviour on the basis of the theory of atomic structure is given on p. 435.

Radioactivity

In 1896 Becquerel found that uranium salts affected a photographic plate through a layer of black paper, and could also discharge an electroscope. Thorium compounds were found by Schmidt and by Mme. Curie in 1898 to possess similar properties (Soddy, *The Interpretation of the Atom*, 1932). The substances were called **radioactive**, from their property of emitting radiations of the kind described below. In the study of radioactivity (Hevesy and Paneth, *A Manual of Radioactivity*, Oxford, 1938) the following methods are available :

(1) The action on a photographic plate.

(2) The phosphorescence produced in platinocyanides, willemite (zinc silicate), kunzite (lithium aluminium silicate), and Sidot's blende (zinc sulphide).

(3) The ionisation of gases by the rays.

The most convenient is the third method. The ionisation, which makes the gas conducting, is detected and measured by a gold-leaf electroscope (Fig. 104). The gold-leaf *G* is attached to the rod *R*, supported by a horizontal rod *K* insulated on blocks of sulphur *S*, and terminating in a metal plate *B*. Below is a metal plate *A*, on which the material to be tested is placed. The gold leaf is given a charge through the wire *M*, which is insulated in a sulphur stopper and can be swung away from the rod *R* when the latter is charged. If the substance *C* is radioactive, the air between the plates *A* and *B* becomes conducting, and the charge leaks away at a rate which may be measured by the fall of the gold leaf, observed through a micrometer eyepiece. The electroscope is much the most sensitive analytical instrument known, since 10^{-12} gm. of radioactive material can easily be recognised.

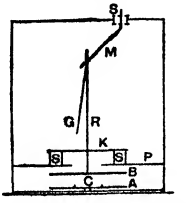


FIG. 104.—Gold-leaf electroscope.

The scintillation method, based on (2), has also been used. When α-rays from a fragment of radium *A* (Fig. 105) strike a phosphorescent screen *B*, each particle produces a flash or scintillation of light visible in a lens *C*. This apparatus, called a **spinthariscope** (Greek *spinther*, a spark), was devised by Crookes in 1903, and by its use individual α-particles can be counted.

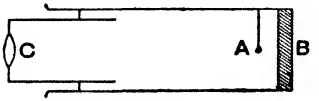


FIG. 105.—Spinthariscope.

Radium.—By the ionisation method Mme. Curie in 1898 found that the uranium ore *pitchblende* (mostly U_3O_8) is more active for a given weight of uranium than a pure uranium salt, and she suspected the presence of a new element more radioactive than uranium. By chemical separation she isolated preparations containing two radioactive elements which she called **polonium** and **radium**, and a third called **actinium** was discovered by her collaborator Debierne. Radium had an activity a million times that of uranium and in highly purified specimens this activity is doubled (Mme. Curie, *Chem. News*, 1903, **88**, in fifteen parts). The radium was separated from the barium, with which it was

isolated, by many fractional crystallisations of the chlorides; Giesel (1902) found that with the bromides eight crystallisations suffice.

In the extraction of uranium the pitchblende is roasted with sodium carbonate and digested with dilute sulphuric acid, when the uranium goes into solution. The residue is boiled with sodium hydroxide solution and washed with water, and the insoluble part treated with hydrochloric acid, which dissolves most of it to form a solution *A*. The small insoluble residue is boiled with sodium carbonate solution to convert sulphates into carbonates, which are purified and dissolved in dilute hydrobromic acid. On evaporation and addition of hydrobromic acid barium and **radium** bromides deposit and are separated by fractional crystallisation, radium bromide being less soluble. From the solution *A* hydrogen sulphide precipitates bismuth and **polonium** (0·004 mg. per ton of pitchblende), and from the oxidised filtrate ammonia precipitates ferric hydroxide containing the **actinium**.

Colorado *carnotite* (p. 644) with 5–10 mg. Ra per ton was formerly used as a source of radium. It was superseded by pitchblende from the Belgian Congo, but the richest deposits of radium-bearing pitchblende (150 mg. Ra per ton) are in the Great Bear Lake territory in N.W. Canada.

Radium is an element of Group II and its compounds are isomorphous with those of barium. Radium salts when pure are colourless, but if they contain barium they are pink. The chloride melts at a high temperature and solidifies to a glassy mass which, unlike the hydrated salt, emits an intense bluish-violet light. The salts ozonise air and shine in the dark with a green phosphorescent glow. In solution in water they form hydrogen peroxide and evolve hydrogen and oxygen. Glass is coloured violet or brown by radium rays, but the colour is discharged by heating nearly to the softening point. In the Bunsen flame radium compounds give a fine carmine tint and the spectrum resembles those of the other alkaline-earth metals. Radium sulphate is even less soluble than barium sulphate, since the element has a higher atomic weight than barium. From the ratio $RaCl_2 : RaBr_2$ Hönigschmid (1912–13) found Ra = 225·97.

Metallic radium was obtained (Mme. Curie and Debierne, 1910) by electrolysing a solution of the chloride with a mercury cathode and separating the mercury from the amalgam by distillation, or by decomposing radium azide $Ra(N_3)_2$ at 180°–250° (Ebler, 1910). Radium is a white metal, m.p. 960°, which rapidly tarnishes in the air, forming a nitride, and decomposes water with evolution of hydrogen.

α-, β-, and γ-Rays.—By interposing sheets of metal foil and superposing powerful magnetic fields in the electroscopic method, it was found that radium emits **three kinds of rays** (Fig. 106):

1. The **α-rays**: positively charged particles, easily absorbed by thin metal foil, and having a limited range in air (7 cm. when emitted from RaC′, a product of disintegration of radium).

2. The **β-rays**: negatively charged particles identical with free negative electrons, emitted with speeds approaching the velocity of light and often capable of penetrating thin sheets of aluminium.

3. The **γ-rays**: not deflected by magnetic fields, consisting of waves identical with very short X-rays (wave-length, $1{\cdot}3 \times 10^{-7}$ to 7×10^{-10} mm., or 1300 – 7 X.U., where 1 X.U. $= 10^{-10}$ mm.), and capable of penetrating several cm. of lead.

The deflections produced by a magnetic field are seen in Fig. 106 to be in opposite directions with the α- and β-rays: the γ-rays are undeflected. The α-rays have a shorter range than the β-rays, and they are less easily deflected.

The phosphorescence effects of radium are mainly due to the α-rays, which on account of their relatively large mass and high velocity ($\frac{1}{15}$ to $\frac{1}{10}$ that of light) possess considerable kinetic energy. In the spinthariscope (p. 195) the impact of each α-particle on the zinc sulphide screen produces a bright flash, and in this way a direct counting of the particles is possible.

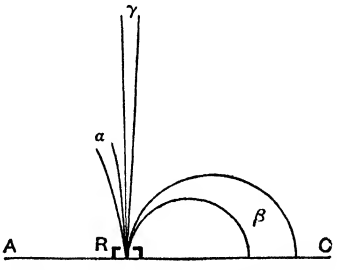


FIG. 106.—Magnetic deflection of α- and β-rays.

The α-particle was shown as follows to be a helium atom with a *positive* charge of two electron units (more accurately a helium nucleus, *i.e.* a helium atom which has lost two electrons):

(1) Rutherford found the ratio e/m (charge/mass) $= 4{\cdot}82 \times 10^{4}$ coulombs per g., almost exactly half that for the hydrogen ion, and Rutherford and Geiger determined e by measuring the charge carried by a counted number of α-particles as $3{\cdot}1 \times 10^{-10}$ cmb., hence the mass $m = 0{\cdot}66 \times 10^{-23}$ g., or about four times that of the hydrogen atom, $1{\cdot}6 \times 10^{-24}$ g. Hence the atomic weight is 4, the same as that of helium.

(2) Ramsay and Soddy (1903) showed that helium is spontaneously formed from radium emanation (p. 198), which emits α-particles. Rutherford and Royds (1908) sealed radium emanation in a very thin glass tube, through which the α-particles passed, and detected the helium spectrum in an outer originally vacuous glass tube.

(3) 1 g. of radium free from its disintegration products emits $1{\cdot}165 \times 10^{18}$ α-particles in a year, and forms 0·043 c.c. of helium. This gives $2{\cdot}7 \times 10^{19}$ atoms per c.c. of helium, in good agreement with the value $2{\cdot}69 \times 10^{19}$ (p. 32).

The speed of α-particles emitted by radium is about 2×10^{9} cm. per sec., hence the kinetic energy of each is $1{\cdot}36 \times 10^{-5}$ erg, or $2{\cdot}4 \times 10^{8}$ times that of a gas molecule at 0°. This large energy accounts for the phosphorescence effects and for most of the heat evolved by radium, which amounts to 25·5 g. cal. per g. of radium per hour.

Although the β-rays are more penetrating to matter in bulk than the α-rays, on account of their smaller size and higher velocity, yet they are more deflected in their encounters with individual atoms than are α-rays. Their paths, therefore, deviate very much from straight lines, as has been shown by the Wilson method (p. 199): they are frequently deflected through 180°. On account of

its smaller mass and kinetic energy, a β-particle produces much less ionisation for 1 cm. path in a gas than an α-particle; the γ-rays ionise by way of the β-rays they first produce.

Radium emanation.—Radium emits a gas called the *emanation*, which may be swept away by a current of air and condensed in a tube cooled in liquid air. By weighing 0·1 cu. mm. or about 0·001 mg. of radium emanation on the micro-balance its atomic weight (on the assumption that it is monatomic) was found by Ramsay and R. W. Gray in 1911 to be 222·4. It is an inert gas belonging to the argon group. It liquefies when at low partial pressures with great sharpness between $-152°$ and $-154°$; the liquid boils at $-65°$ and solidifies at $-71°$. Under the microscope the liquid is colourless and transparent, whilst the solid is opaque. In a glass tube the liquid glows with great brilliancy with a steel-blue light which at lower temperatures changes to brilliant orange-red. Ramsay, therefore, proposed for the gas the name niton (Latin *nitidus* = shining), but the name **radon** (proposed by Schmidt in 1918) is now used. Radon has a characteristic spectrum similar to that of xenon, and is distinctly soluble in water. It is strongly adsorbed by charcoal at low temperatures.

The unit of radioactivity is the *curie*, which is the activity of 0·63 cu. mm. of emanation in equilibrium with 1 g. of radium.

If it is assumed that the radium atom breaks down into an α-particle and a radon atom, the atomic weight of radon should be $Ra(226) - He(4) = 222$, whilst the observed value is 222·4, in very good agreement.

Atomic disintegration.—That the heat emitted by radium (which comes mostly from the large kinetic energy of the α-particles) might be due to a spontaneous disintegration of the radium atoms was tentatively suggested by Mme. Curie in 1900, and this theory of **atomic disintegration** was definitely advanced, on the basis of experiment, by Rutherford and Soddy in 1903. The radium atom is assumed first to disintegrate into a helium atom (α-particle) and the gaseous emanation (radon). Radon is also radioactive, emitting α-particles and forming a solid *active deposit*, which is assumed to disintegrate in turn in successive stages, each accompanied by the emission either of α-rays, or of β-rays and γ-rays, producing in succession Ra-A, Ra-B, Ra-C, Ra-D, Ra-E, Ra-F and Ra-G. Altogether five α-particles and five β-particles are emitted between Ra and Ra-G (which is inactive), and hence the atomic weight of Ra-G should be $Ra - 5He = 226 - 20 = 206$, which is approximately the atomic weight of lead. Radium-G is an isotope of lead.

In the radioactive disintegration of thorium (p. 202), six α-particles are emitted, hence the final inactive product Th-D has an atomic weight of $232 - 24 = 208$, and is another isotope of lead.

The lead from uranium minerals (which is derived from radium) and that from thorium minerals were found in 1914 by Soddy and Hyman, and by Richards and Lembert, to have different atomic weights, that of uranium lead being approximately 206 and that of thorium lead approximately 208. This is a striking confirmation of the theory of radioactive disintegration:

		Pb
Uranium minerals	East African pitchblende	206·05
	Bröggerite	206·06
	Cleveite	206·08
Thorium minerals	Thorianite (containing also 26·8 p.c. U)	206·83
	Thorite (30·1 p.c. Th ; 0·45 p.c. U)	207·90
Ordinary lead		207·21

The activity of radium is unaffected by temperature, and is the same at a red heat as at the temperature of liquid air. Radioactivity thus differs from ordinary chemical changes, the velocity of which is largely affected by temperature.

The *fraction* of the total number of atoms of a radioactive element disintegrating per sec. is constant, so that the activity diminishes exponentially with the time :

$$N_t = N_0 e^{-\lambda t},$$

where N_0, N_t are the numbers of atoms present at the beginning and after t secs., and λ is the *disintegration* (or *decay*) *constant.*

The inverse of the fraction disintegrating in unit time is the *average life* $\tau = 1/\lambda$, and the period in which half the atoms have disintegrated is the *half-life* T, where $T = 0{\cdot}693/\lambda$. Each radio-element is characterised by its half-life, which varies from some million-millionths of a second for very unstable elements (10^{-11} sec. for ThC′) to thousands of millions of years for stable elements (2×10^{10} years for Th). When a parent element is producing decay products at the same rate as these are undergoing further change, a state of *radioactive equilibrium* is set up, in which the amounts of parent substance and its decay products are in the ratio of their average lives.

A relation between λ and the range R of the α-particles emitted is the *Geiger-Nuttall equation* (1911) :

$$\log \lambda = A + B \log R,$$

where the constants are $B = 59$ and $A = -42$, -44, and -46, for the uranium, thorium, and actinium series, respectively. Actually, the α-particles from some radio-elements have not all the same energy or range, but the α-radiation has a " fine structure " or " energy spectrum " corresponding with energy levels in the nucleus (Gamow, *Structure of Atomic Nuclei and Nuclear Transformations*, 1936 ; Feather, *Nuclear Physics*, 1936).

Deflection of α-rays in gases.—The α-particle passing through air or other gas produces gaseous ions which can act as centres for the deposition of moisture. If the air saturated with water vapour is suddenly cooled by expansion the paths of the α-rays become visible in strong light as lines of droplets of water condensed on the gaseous ions, and these " cloud tracks " can be photographed (C. T. R. Wilson, *Proc. Roy. Soc.*, 1911, **85**, 285).

A diagram of the Wilson apparatus (Fig. 107) shows a fixed cylinder A surmounted by a glass ring G covered with a glass plate g, on the underside of which is moistened gelatine. The movable glass cylinder P, covered at the top with

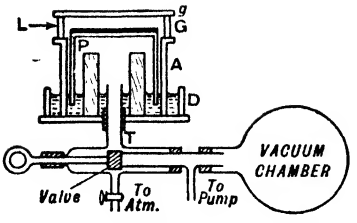


FIG. 107.—Wilson cloud chamber.

moistened black gelatine, dips into water in the dish *D*. The tube *T* is connected with a valve communicating with an evacuated vessel. By opening this valve, *P* descends suddenly and causes adiabatic expansion and cooling of the moist air in *G*. If nuclei are present, drops of water condense on them. The chamber is brightly illuminated from *L* and a photograph of the fog tracks against the black ground is taken through *g*. Many ingenious modifications of Wilson's apparatus have been devised, *e.g.* by Shimizu (1921) and Blackett (1922), but the principle is the same.

The paths of two single α-particles are shown in Fig. 108. The left-hand track shows a large deflection at its end, where it has struck an atom of gas, and a small spur going off in the other direction, representing the recoiling atom. From the angle between the spur and the original direction of the α-particle the relative masses of the two particles can be calculated from the laws of elastic collision (oxygen $16{\cdot}72 \pm 0{\cdot}42$; helium 4·03). This method gives the masses of single atoms (Blackett, 1922).

FIG. 108.—Tracks of two α-rays (enlarged).

ATOMIC STRUCTURE

The nuclear atom.—The large deflection suffered by an α-particle at the end of its track suggests that its positive charge approaches close to some positive charge concentrated into a small space in the atom, thus setting up a powerful repulsive force. The α-particle must pass through several atoms in its path before it encounters, in one particular atom, this small concentrated positive charge. Calculations from the deflections by the inverse square law suggest that the two charges approach within a distance of 10^{-12} cm., much smaller than the atomic radius of about 10^{-8} cm.

Rutherford in 1911 developed an atom model suggested by Nagaoka in 1904, in which the atom is a kind of minute planetary system of a small *positive nucleus* surrounded by electrons which neutralise the positive charge and revolve around the nucleus at a relatively large distance from it. Except in the simplest atoms, hydrogen and helium, these electrons occupy successive *orbits* or *shells*, the radius of the outer shell being of the order of the radius of the atom. Most of the volume of the atom is thus empty space. Since the electrons have a very small mass, most of the mass of the atom resides in the very small positive nucleus. This simple theory has since been much elaborated and modified, but the fundamental idea of the nucleus and outer electrons remains broadly acceptable.

The series of *atomic numbers* determined by Moseley (p. 192) was interpreted by him (1913–14) and by van den Broek (1913) as follows: (i) the atomic number represents the positive nuclear charge in electron units, (ii) successive atoms counting from hydrogen have positive nuclear charges increasing in steps of one unit for each unit increase in atomic number.

This agrees with the measurements of the deflection of α-particles by atoms.

Geiger and Marsden (1913) by using the scintillation method found that many α-particles pass through thin (0·01 mm.) gold leaf without much deviation, but some are deflected through large angles and may even return towards the incident side. The positive α-particle, it is assumed, may sometimes approach very close to the small positive nucleus of the gold atom, and then experiences a strong repulsion. Chadwick (1920) by this method calculated the charge on the nucleus of the metal atom, which agrees closely with the atomic number (given in brackets): Pt 77·4 (78), Ag 46·3 (47), Cu 29·3 (29).

The simplest atom, the hydrogen atom, is assumed to consist of a very small positive nucleus called a **proton** and a single electron of equal negative charge situated at a relatively large distance (10^{-8} cm.) from the proton. The positive charge of *any* atomic nucleus is assumed to be due to protons contained in it. The mass of the proton is very nearly the same as that of the neutral hydrogen atom (since the electron has only a very small mass), hence the mass due to the p protons (p = atomic number of the element) can be found. Except in the case of hydrogen (the nucleus of which is a single proton) this is less than the total mass A of the atom. The balance is supposed to be made up by n electrically neutral particles called **neutrons** in the nucleus, each of approximately the same mass as the proton. Thus the nucleus has a mass $A = (p + n)$ and a positive charge p. In the neutral atom there will be p outer electrons. The helium nucleus or α-particle has a mass 4 and charge 2, hence it contains two protons and two neutrons. The nuclei of the three isotopes of oxygen of masses 16, 17 and 18 all contain 8 protons, since they all have the same atomic number 8, and hence 8, 9 and 10 neutrons, respectively.

Free **neutrons** of mass 1 and charge 0, denoted by ${}_0^1n$, are emitted when some light elements such as beryllium are bombarded with α-rays (Bothe and Becker, 1930; Chadwick, 1932). The participation of neutrons in nuclear structure was postulated by Heisenberg (1932) and Majorana (1933). The existence of neutrons was predicted by Rutherford in 1920. They are also liberated in other nuclear changes (p. 205).

It is usually assumed that the protons and neutrons in the nucleus are as far as possible combined in the form of α-particles (2 protons + 2 neutrons). In some cases, however, the α-particles emitted from a nucleus must be formed at the moment of emission; in the disintegration of a lithium nucleus by proton bombardment (p. 207) two α-particles are emitted and both these (mass 8) could not have existed in the lithium nucleus (mass 7).

The nucleus of an atom has a resultant moment of angular momentum due to the spins of the protons and neutrons, each contributing $\frac{1}{2}$ a unit. This angular momentum of the nucleus can be determined from the changes of hyper-

fine structure of spectrum lines in a magnetic field, and its values show that electrons cannot be present in atomic nuclei. The ^{14}N nucleus has a total moment of 1 unit, corresponding with 7 protons and 7 neutrons, making up an even number 14 of particles, whilst if it were composed of 14 protons and 7 electrons making up an odd number 21 of particles its total moment would be an odd multiple of $\frac{1}{2}$, *i.e.* half integral. The odd-number isotopes of cadmium, mercury and lead would have an odd number of electrons and an even total number of particles in the nuclei, yet their total moment is half integral.

The Chemistry of the Radio-elements

The radioactivity of uranium.—In 1900 Crookes found that on treating a uranium salt with ammonium carbonate a slight residue is left in which all the photographic activity of the uranium salt is concentrated. The solution emits α-rays, which discharge an electroscope but do not affect a photographic plate, whilst the residue emits β- and γ-rays, which are photographically active. The precipitate contains a radioactive product called **uranium-X** (which is actually a mixture). On standing it becomes inactive, whilst the solution regains its activity and yields another specimen of uranium-X. Uranium is therefore capable of growing uranium-X.

Boltwood, and Soddy (1905), found that radium is spontaneously produced from uranium, but the change is not direct. An intermediate element called **ionium** is formed, which was separated by Boltwood from the uranium mineral carnotite. It is precipitated as oxalate along with its isotope thorium. He also found that uranium in disintegrating emits two kinds of α-particles, which suggests that there are two varieties of uranium, called **uranium-I** and **uranium-II.** U-II passes directly into ionium by emission of an α-particle, whilst U-I passes into U-X_1. From U-X_1 emission of a β-particle gives U-X_2 and U-Z, each of which by emitting a β-particle gives U-II. The complete series of transformations of uranium, which includes that of radium, is shown in the table on p. 204. The final product, RaG, is an isotope of lead (uranium lead) of mass 206.

Each disintegration product is an isotope of some common element shown at the foot of the table, *e.g.* ThC, AcC, RaE and RaC are isotopes of bismuth.

The radio-element **polonium**, discovered in pitchblende by Mme. Curie, is RaF, one of the disintegration products of radium, and is isotopic with other disintegration products of radium, thorium and actinium, as shown in the table in Group VIB. Polonium is deposited from solutions on a rod of bismuth, copper, silver or nickel, and is also quantitatively precipitated by stannous chloride. Radium-D (a lead isotope) emits β-rays giving radium-E (a bismuth isotope) and this emits β-rays giving radium-F or polonium, so that lead from uranium minerals may be used as a source of polonium, which is separable by the above method. Alternatively the active deposit in old radon tubes may be used. Polonium has a relatively short life but furnishes a source of α-particles free from other radiations, as it passes directly into inactive Ra-G (lead).

The radioactivity of thorium.—In 1902 Rutherford and Soddy found that thorium emits a gaseous radioactive emanation, now called *thoron*. After pre-

cipitation of thorium hydroxide by ammonia from a thorium salt solution, the filtrate contained a very active substance called **thorium-X**. After a month's time the Th-X completely lost its activity, whilst the precipitate of thorium hydroxide recovered exactly the activity of the original thorium salt, *i.e.* the activity which had been lost by the Th-X. It was shown by Hahn (1905–11) that Th-X is formed from thorium through three intermediate products called **mesothorium-I, mesothorium-II,** and **radiothorium**. From radiothorium (Ra-Th), Th-X, Th emanation, Th-A, Th-B and Th-C are formed. The Th-C atoms may disintegrate in two ways. About one-third emit α-rays forming Th-C″, which then emits β-rays forming Th-D, whilst two-thirds of the Th-C atoms emit β-rays forming Th-C′, which then emits α-rays forming Th-D. Thorium-D is an isotope of lead of mass 208. No detectable rays are emitted by mesothorium-I, so that the production of mesothorium-II is called a "rayless change," but probably feeble β-rays are emitted.

The actinium series.—In 1899 Debierne separated with the iron precipitate from pitchblende residues a preparation of an active substance which he called **actinium**. The immediate parent of actinium is an element discovered in 1917 by Soddy and called by him eka-tantalum, and independently by Hahn and Meitner, who called it **protoactinium** (also called *protactinium*). This is formed by β-ray change from an isotope of U-X_1 called **uranium-Y**, discovered by Antonoff in 1911, which is an isotope of thorium, and may be derived from U-II or from another uranium isotope U = 235 called **actinouranium**. Protoactinium, which forms actinium by emission of an α-particle, although an element of Group V, is chemically more similar to thorium and zirconium rather than to tantalum, and it has been extracted in relatively large amounts from pitchblende by von Grosse (1935) and its atomic weight found by chemical methods. The final product of disintegration of the actinium series is Ac-D, an isotope of lead of mass 207.

The Russell-Soddy displacement law.—The *position of an element in the periodic table* is fixed by its atomic number, which is equal to the positive charge on the atomic nucleus measured in terms of the electronic charge as unit. The atomic numbers of uranium, thorium, and radium are known from the positions of these elements in the periodic table, and the atomic numbers of all their disintegration products may be calculated by subtracting 2 for every α-particle emitted (loss of nuclear charge $+2$) or adding 1 for each β-particle emitted (loss of nuclear charge -1). The positions of the radio-elements in the periodic table are thus fixed by a simple law, stated by A. S. Russell and by Soddy in 1913:

(i) In an *α-ray change* the product generated falls into a group of the periodic table *two places lower* than that containing the parent substance.

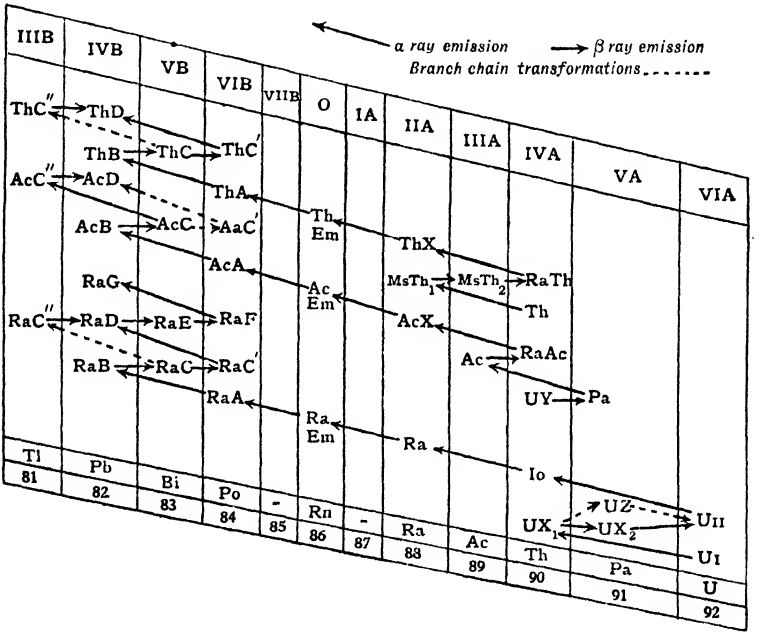
(ii) In a *β-ray change* the product falls into a group of the periodic table *one place higher* than that containing the parent substance.

Ra (Group II) emits an α-particle and forms the inert gas radon (Group O). Ra-D (Group IV) emits a β-particle and forms Ra-E (Group V), etc.

Since the atomic nucleus is supposed to contain only protons and neutrons, the expulsion of a β-ray electron is supposed to involve the transformation in the nucleus of a neutron into a proton and an electron.

Each element occurring in a vertical column in the table below belongs to the group of the periodic system shown at the top and has the atomic number shown at the foot. All the elements with the same atomic number occupy the same place in the periodic table, which may also be occupied by the common

TABLE OF RADIO-ELEMENTS



element shown at the foot. These elements are *isotopes* and are chemically inseparable from one another. The radioactive isotopes are, however, distinguishable by their disintegration constants and by the nature of the elements from which they are derived or of the products to which they give rise. Isotopes are also differentiable by their atomic weights (*e.g.* ^{206}Pb and ^{208}Pb) and their densities, since their atomic volumes are identical. The *molecular* solubilities of their compounds are identical; those of common lead nitrate and uranium lead nitrate are 1·7993 and 1·7991 mol/lit., respectively, whilst the weights of lead per 100 g. of water are 37·281 and 37·130 g., substantially in the ratio of the atomic weights. The X-ray spectra of lead isotopes (depending on the atomic numbers) are identical within 0·0001 A., but the arc spectra differ by about 0·005 A. (Merton, 1919).

Nuclear Chemistry

Nuclear transformations.—The collision of swift α-particles, protons (hydrogen nuclei), deuterons (deuterium nuclei, mass 2, charge 1) or neutrons, with atoms of other elements may cause the ultimate disruption of the nucleus of the atom struck and the ejection of fragments of the atom with such speeds that their presence may be detected by the scintillation or the cloud-track methods.

Rutherford (1919), extending an observation made by Marsden (1914), found that the protons ejected by α-particles (from Ra-C) from hydrogen atoms by collision had a range of about 28 cm. in air (as determined by the scintillation method), as compared with the range of the α-particle in air of about 7 cm. The identity of the long-range particles with protons was established by the measurement of e/m by deflection in electric and magnetic fields. He found that very long-range protons (40 cm.) were formed in nitrogen.

Rutherford, partly in collaboration with Chadwick (1921; *J.C.S.*, 1922, **121**, 400), showed that long-range protons are also produced by the bombardment of boron, fluorine, sodium, aluminium, phosphorus, and chlorine, by α-rays, and thus gave a proof that the nuclei of these atoms contain protons, and the first definite case of *artificial* disintegration. The actual number of atoms disintegrated is exceedingly small.

Blackett (1922) by the cloud-track method obtained photographs of collisions involving the expulsion of protons from atoms. When α-particles (mass 4, nuclear charge 2) bombard nitrogen atoms (mass 14, nuclear charge 7) they apparently enter the nucleus of the atom, producing a particle of mass $14+4=18$ and nuclear charge $7+2=9$, *i.e.* an isotope of fluorine. This nucleus then emits a proton (mass 1, charge 1), leaving a nucleus of mass $18-1=17$ and charge $9-1=8$, *i.e.* an isotope of oxygen. The end of the α-ray track shows only two prongs, corresponding with the formation of a proton and the new nucleus. This artificial building up of an element (oxygen) from a lighter element (nitrogen) may be represented as follows, the lower figures giving the charges and the upper the masses of the nuclei:

$$^{14}_{7}\mathrm{N} + ^{4}_{2}\mathrm{He} = ^{17}_{8}\mathrm{O} + ^{1}_{1}\mathrm{H}.$$

Artificial radioactivity.—In 1933 Joliot and Mme. Curie-Joliot found that both positive and negative electrons are emitted by thin layers of beryllium, boron and aluminium bombarded by α-particles from polonium, and in 1934 they found that the emission of positive electrons persists after the removal of the source of α-particles. This was the first observed case of *artificial radioactivity*. Since then the subject has been studied by numerous workers, who have also used bombardment with fast protons, deuterons and neutrons. The neutrons, being uncharged, readily enter the positive nuclei.

In the bombardment of aluminium, the α-particle enters the nucleus, forming an unstable isotope of phosphorus, which then disintegrates with the emission of a positive electron, and thus behaves as an artificial radioactive element with a characteristic half-life. In what follows the neutron is

denoted by ${}_0^1n$, the negative electron by β^-, the positive electron by β^+, the α-particle by ${}_2^4\mathrm{He}$, and D and T denote the deuterium (^{2}H) and tritium (^{3}H) nuclei. Neutrons are formed by the action of α-rays on beryllium, when presumably carbon is also produced:

$$ {}_4^9\mathrm{Be} + {}_2^4\mathrm{He} = {}_6^{12}\mathrm{C} + {}_0^1n, $$

and by other processes. In the Joliot experiment radio-phosphorus is formed by reaction A and then disintegrates by reaction B, forming an isotope of silicon:

$$ (A)\ {}_{13}^{27}\mathrm{Al} + {}_2^4\mathrm{He} = {}_0^1n + {}_{15}^{30}\mathrm{P}, \qquad (B)\ {}_{15}^{30}\mathrm{P} = \beta^+ + {}_{14}^{30}\mathrm{Si}, $$

On dissolving the irradiated aluminium in hydrochloric acid the hydrogen evolved is radioactive, presumably from radio-phosphine content. On dissolving the aluminium in aqua regia and adding sodium phosphate and a zirconium salt, the zirconium phosphate precipitate carried all the activity. These chemical methods of recognising artificially-formed radio-elements are important, and since isotopes have the same chemical reactions, the radio-elements have been extensively used as " indicator elements " in studying the mechanism of chemical reactions (von Hevesy, *J.C.S.*, 1939, 1213), *e.g.* radio-phosphorus in biological metabolism, and radio-carbon in photosynthesis in plants.

When carbon is bombarded with deuterons radio-nitrogen is formed:

$$ {}_6^{12}\mathrm{C} + {}_1^2\mathrm{D} = {}_0^1n + {}_7^{13}\mathrm{N}. $$

The bombarded carbon when burnt in a mixture of helium and air forms a gas containing radio-nitrogen. Oxygen and carbon dioxide are removed by alkaline pyrogallol and the residual gas, which retains all the radioactivity, is passed into a vacuous tube containing heated calcium. The residual gas, mainly helium, is pumped off and by adding water to the calcium a strongly radioactive ammonia is evolved. Measurements of the half-life of the active gas at various stages gave a constant value of 10·5 min., showing that a single element was concerned (Yost, etc., 1935).

Some artificial radio-elements emitting positive electrons are: ^{11}C, ^{13}N, ^{15}O, ^{17}F, ^{26}Al, ^{27}Si, ^{34}Cl, ^{43}Sc; some emitting negative electrons are ^{8}Li, ^{12}B, ^{14}C, ^{16}N, ^{19}O, ^{20}F, ^{27}Mg, ^{28}Al, ^{31}Si, ^{32}P, ^{35}S, ^{42}K, ^{134}Cs, ^{140}La, ^{198}Au (the dream of the alchemists having thus been realised).

The disintegration of nuclei by γ-rays has also been observed (Chadwick, etc., 1934 f.):

$$ {}_1^2\mathrm{D} + h\nu = {}_1^1\mathrm{H} + {}_0^1n, $$
$$ {}_4^9\mathrm{Be} + h\nu = {}_4^8\mathrm{Be} + {}_0^1n, $$

where $h\nu$ denotes the energy quantum (photon) conveyed by the γ-ray. Known radio-elements have also been synthesised, *e.g.* RaE by bombarding bismuth with deuterons (Livingwood, 1936).

In the detection of artificial radioactivity the **Geiger-Müller counter** is used. This is a thin metal tube (penetrated by electrons or positrons) with an axial insulated wire and filled with air at 80 mm. pressure. The tube is at a high

potential of 1000–15,000 volts and the wire is connected with a valve amplifier. An electron or positron entering the tube produces a few gaseous ions which move with high velocity towards the wall or the wire (according to their charge) and generate more ions by collision. The ionisation process is cumulative, so that finally a discharge occurs across the air and the impulse is transmitted to the amplifying system.

Fast protons or deuterons for atomic bombardment are produced in a **cyclotron,** devised by Lawrence and co-workers and shown in plan in Fig. 109. The two semicircular flat brass boxes *A* and *B* with their edges separated by a narrow slit *a* are supported horizontally inside an evacuated brass container. A strong magnetic field acts at right angles to the plane of the boxes, which are connected to a source of high-frequency oscillations of high voltage. Protons or deuterons are generated at the centre by a hot filament *F* in hydrogen or deuterium at low pressure, and are accelerated by the electric field into one box, say *A*, being bent into a nearly circular path by the magnetic field. The time taken to traverse the semicircle *A* is adjusted so that when the particle comes back to the slit *a* the field between *A* and *B* is reversed and the particle is accelerated into *B*, and so on. The circular path increases in size because the velocity of the particle increases. Finally the particle passes through a small slit at *S* into a chamber containing the material to be bombarded, being turned out of its circular path by a positively charged deflector *D*. *S′* and *S″* are metal screens protecting from the high potential the target chamber and the Geiger-Müller counter *G* separated from the target by mica windows.

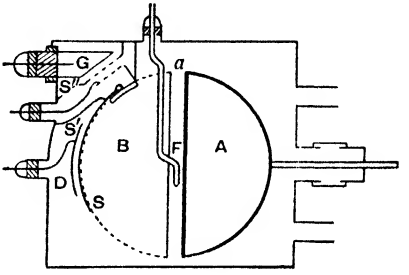


FIG. 109.—Cyclotron.

Of the very large number of atomic transformations brought about by protons, deuterons, α-particles and neutrons (Seaborg, *Chem. Reviews*, 1940, **27**, 199), the following may be mentioned:

$$^{7}_{3}\mathrm{Li} + {}^{1}_{1}\mathrm{H} = {}^{4}_{2}\mathrm{He} + {}^{4}_{2}\mathrm{He}$$
$$^{6}_{3}\mathrm{Li} + {}^{1}_{0}n = {}^{4}_{2}\mathrm{He} + {}^{3}_{1}\mathrm{T}$$
$$^{10}_{5}\mathrm{B} + {}^{1}_{0}n = {}^{4}_{2}\mathrm{He} + {}^{4}_{2}\mathrm{He} + {}^{3}_{1}\mathrm{T}$$
$$^{23}_{11}\mathrm{Na} + {}^{1}_{0}n = {}^{1}_{1}\mathrm{H} + {}^{23}_{10}\mathrm{Ne}$$

$$^{6}_{3}\mathrm{Li} + {}^{1}_{1}\mathrm{H} = {}^{4}_{2}\mathrm{He} + {}^{3}_{2}\mathrm{He}$$
$$^{9}_{4}\mathrm{Be} + {}^{1}_{1}\mathrm{H} = {}^{6}_{3}\mathrm{Li} + {}^{4}_{2}\mathrm{He}$$
$$^{2}_{1}\mathrm{D} + {}^{2}_{1}\mathrm{D} = {}^{3}_{1}\mathrm{T} + {}^{1}_{1}\mathrm{H}$$
$$^{127}_{53}\mathrm{I} + {}^{1}_{0}n = {}^{128}_{53}\mathrm{I}$$
$$^{9}_{4}\mathrm{Be} + {}^{2}_{1}\mathrm{D} = {}^{10}_{5}\mathrm{B} + {}^{1}_{0}n$$

In some cases alternative changes occur:

$$^{14}_{7}\mathrm{N} + {}^{1}_{0}n = \begin{cases} {}^{11}_{5}\mathrm{B} + {}^{4}_{2}\mathrm{He} \\ {}^{14}_{6}\mathrm{C} + {}^{1}_{1}\mathrm{H} \\ {}^{7}_{3}\mathrm{Li} + 2{}^{4}_{2}\mathrm{He} \end{cases}$$

$$^{6}_{3}\mathrm{Li} + {}^{2}_{1}\mathrm{D} = \begin{cases} {}^{4}_{2}\mathrm{He} + {}^{4}_{2}\mathrm{He} \\ {}^{7}_{3}\mathrm{Li} + {}^{1}_{1}\mathrm{H} \\ {}^{7}_{4}\mathrm{Be} + {}^{1}_{0}n \end{cases}$$

Radio-sodium with a relatively long life and intense β-ray and γ-ray emission

is formed by bombarding sodium chloride with high-energy deuterons, and may become of technical importance :

$$^{23}_{11}\mathrm{Na} + ^{2}_{1}\mathrm{D} = ^{1}_{1}\mathrm{H} + ^{24}_{11}\mathrm{Na}$$
$$^{24}_{11}\mathrm{Na} = ^{24}_{12}\mathrm{Mg} + \beta^{-} + h\nu.$$

The supposed formation of " transuranic " elements of atomic number greater than that of uranium by bombar ding uranium with neutrons (Fermi, 1934) has received another explanation ; the uranium nucleus is disrupted and various lighter elements are formed (Meitner and Frisch, 1939 ; *Ann. Rep. C.S.*, 1939, 11 f.).

Some determinations of the atomic masses of isotopes have been made by measuring the energy liberated in disintegration by incident particles and subtracting the mass equivalent of this energy given by Einstein's equation $\Delta E = mc^2$ (p. 2).

The Electronic Structure of Atoms

The positive charge of the atomic nucleus increases by 1 unit by addition of a proton for each successive step in atomic number. The mass of the nucleus increases, usually by more than 1 unit, by addition of protons and neutrons. The structures of atoms from hydrogen to argon can be represented as follows :

	Mass of nucleus	*Charge on nucleus*	*Outer electrons*		*Mass of nucleus*	*Charge on nucleus*	*Outer electrons*
H	1	1	1	Ne	20	10	2+8
He	4	2	2	Na	23	11	2+8+1
Li	7	3	2+1	Mg	24	12	2+8+2
Be	9	4	2+2	Al	27	13	2+8+3
B	11	5	2+3	Si	28	14	2+8+4
C	12	6	2+4	P	31	15	2+8+5
N	14	7	2+5	S	32	16	2+8+6
O	15	8	2+6	Cl	35	17	2+8+7
F	19	9	2+7	A	40	18	2+8+8

When a 2-electron shell is completed with helium, a new shell begins to form outside it, containing from 1 electron in lithium to 8 electrons in neon. The structure of the next period of atoms higher than neon is a repetition of this, a new shell of 8 electrons being completed with the next inert gas, argon.

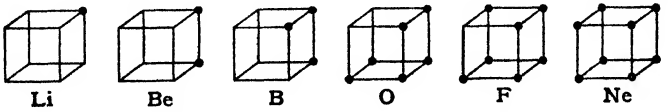


Fig. 110.—Structure of atoms on the octet theory.

The outer shells of all the inert gas atoms contain 8 *electrons*, and this stable grouping of an **octet** of electrons originally suggested an arrangement at the corners of a cube (G. N. Lewis, *J.A.C.S.*, 1916, **38**, 762). In Fig. 110 the inner shells are supposed to be inside the cubes, only the outer electrons being shown. This actual arrangement is no longer regarded as indicating the actual structure, but it is a useful pictorial approximation.

The eight elements in periods 2 and 3 of the periodic table correspond with the completion, step by step, of two successive shells of 8 electrons around the nuclei. Periods 4 and 5 each contain 18 elements, so that it is supposed that shells of 18 electrons are completed in them. Since the outer shells of krypton and xenon (which close these periods) each contain 8 electrons, there must be completed shells of 18 electrons below them, the original outer shells of argon and krypton thus expanding to 18. The electronic structures of the inert gases are therefore :

He	2
Ne	2 + 8
A	2 + 8 + 8
Kr	2 + 8 + 18 + 8
Xe	2 + 8 + 18 + 18 + 8
Em	2 + 8 + 18 + 32 + 18 + 8

Period 6, if we include the missing element 85, contains 32 elements, hence 32 electrons are added in succession in passing from xenon to the radioactive emanation. In passing through the series of rare earths the *inner* group of 18 electrons of xenon expands to 32, whilst the *outer* group remains as 8 + 3 (or 9 + 2) electrons. This explains why the rare earths all belong to the same group and have the same valency.

The arrangement of electrons around the nuclei of the atoms of the elements is shown in table below.

SHORT TABLE OF ATOMIC STRUCTURES

	0	1 2 3 4 5 6 7	2 2 2 2 2 2 2 2 2	2 2 - 2 2
			9 10 11 12 13 14 15 16 17	9 9 - 9 9 19 20 - 30 31
		H		
2	He	Li Be B C N O F		
2 8	Ne	Na Mg Al Si P S Cl		
2 8 8	A	K Ca		
2 8			Sc Ti V Cr Mn Fe Co Ni Cu	
2 8 18		Zn Ga Ge As Se Br		
2 8 18 8	Kr	Rb Sr		
2 8 18			Y Zr Nb Mo — Ru Rh Pd Ag	
2 8 18 18		Cd In Sn Sb Te I		
2 8 18 18 8	Xe	Cs Ba		
2 8 18 18			La	
2 8 18				Ce - - Yb
2 8 18 32			Lu Hf Ta W Re Os Ir Pt Au	
2 8 18 32 18		Hg Tl Pb Bi Po —		
2 8 18 32 18 8	Em	— Ra		
2 8 18 32 18			Ac Th Pa U	

All elements with the same completed groups of electrons (2, 8, 18 or 32) are shown in the same horizontal row, and the vertical columns contain elements with the same number of electrons in the incomplete *outer* groups, shown at the top. The electronic arrangements are read off as follows :

O 2+6 Ca 2+8+8+2 Fe 2+8+14+2

When scandium is reached, instead of the group 2+8+8+3 being formed, the group 2+8+8 expands to 2+8+9 and 2 electrons form an outer shell. In the ion $Sc^{\cdots}$ these two electrons and one from the inner group are lost, so that the scandium ion has the same outer structure as argon, 2+8+8. The upper limits of covalencies 8, 6 and 4 are marked by heavy horizontal lines. The elements Cr, Cu, Nb, Mo, Ru, Rh and Ag have only one electron in the outer group in the " normal " atom, and in Pd the 2 electrons have joined the group of 16, as shown in the full table on p. 263, but practically all these give bivalent ions, some electrons of a lower group being very easily removed, which is characteristic of transitional elements (p. 261).

The Electronic Theory of Valency

In the simple theory the **valency** of an atom is regarded as a tendency to combine with other atoms and is measured by the number of hydrogen or halogen atoms which one atom of the given element can combine with or replace. Apart from the zero-valent inert gases, atoms can have valencies from 1 to 8 as a maximum (p. 178). In the present section some different types of valency are described, and explained from the point of view of atomic structure.

Electrovalency.—A lithium atom reacts with a fluorine atom to form ions Li^+ and F^- by the transfer of the outer electron of the lithium to the outer shell of 7 electrons of the fluorine. The lithium ion has the electron pair of the helium atom as its outer shell, whilst the fluorine ion has an outer octet of electrons like neon. The change is easily visualised from Fig. 110. The chlorine atom has an inner octet (the neon structure) and 7 outer electrons. The sodium atom has an inner completed octet and 1 outer electron. In the reaction between sodium and chlorine the sodium transfers its outer electron to the chlorine, the ions Na^+ and Cl^- being formed, with the external octets of neon and argon. In such compounds as Li^+F^- and Na^+Cl^- *there is no true valency bond between the ions*, these being held by electrostatic attraction in the lattice (Fig. 144, p. 239), whilst in solution the ions are free. Such a link is sometimes called an **electrovalent link** or an **electrovalency**. It must not be thought of as a definite directed bond between the two ions (Sherman, *Chem. Rev.*, 1932, **11**, 93).

These examples show that atoms can give outer electrons to other atoms, so that each forms a positive or negative ion, respectively, often with an outer octet of electrons. This type of change was emphasised by Kossel (1916).

Covalency.—A second type of bond formation was first suggested by G. N. Lewis (1916), and this leads to the ordinary directed valency bonds in non-ionic compounds.

Lewis assumes that *in the formation of an ordinary single valency bond* (**covalent link** or **covalency**) *a pair of electrons is shared in common by two atoms.* In

this way one or both atoms may complete an octet of outer electrons. The water molecule is formed from the oxygen atom with 6 electrons and two hydrogen atoms each with 1 electron, and the oxygen in water is surrounded by 8 electrons (Fig. 111). The formation of a chlorine molecule from two atoms of chlorine, each with 7 electrons, may be represented by two cubes joined along an edge,

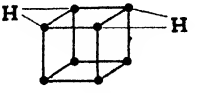


FIG. 111.—Water molecule.

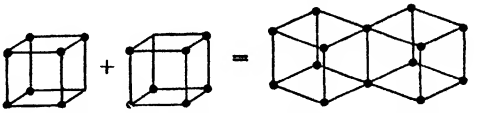


FIG. 112.—Formation of chlorine molecule.

this edge having a shared pair of electrons representing the single bond (Fig. 112). If the outer electrons are represented by dots, each atom of chlorine will be $:\ddot{\underset{\cdot\cdot}{\text{Cl}}}\cdot$ and the chlorine molecule will be $:\ddot{\underset{\cdot\cdot}{\text{Cl}}}:\ddot{\underset{\cdot\cdot}{\text{Cl}}}:$ which is the electronic formula corresponding with the structural formula Cl—Cl.

A *double bond* is formed by *four* equally shared electrons, two from each atom. Fig. 113 shows the formation of carbon dioxide:

$$:\text{C}:+2:\ddot{\text{O}}:=:\ddot{\text{O}}::\text{C}::\ddot{\text{O}}:$$

the double bonds in O=C=O each having four electrons.

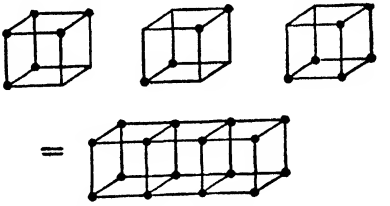


FIG. 113. Formation of carbon dioxide molecule.

A *triple bond* is formed by *six* equally shared electrons, as in the nitrogen molecule : N : : : N : or N ≡ N.

Coordinate links.—Another type of covalent bond formation (G. A. Perkins, *Phillipine J. Sci.*, 1921, **19**, 1; *J.C.S.*, 1922, **122**, ii, 138) is that in which the pair of electrons forming a link comes from *the same atom* (instead of being provided by and equally shared between two atoms), when what is called a **coordinate link** is formed. The simplest case is the formation of the ammonium ion from a proton and a molecule of ammonia:

$$\begin{matrix}\text{H}\\ \ddot{\text{H}}:\ddot{\text{N}}:+\overset{+}{\text{H}}=\\ \ddot{\text{H}}\end{matrix}\left[\begin{matrix}\text{H}\\ \ddot{\text{H}}:\ddot{\text{N}}:\text{H}\\ \ddot{\text{H}}\end{matrix}\right]^{+}$$

Coordinate links are formed when apparently saturated molecules add on other molecules to form what were previously called "molecular compounds."

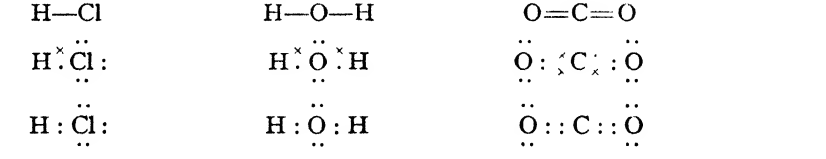
Nitrogen has 5 outer electrons and shares 3 with three hydrogens forming ammonia NH_3, with an outer octet around the nitrogen. Of this octet 2 electrons form a *lone pair, i.e.* are unshared. This pair may be *donated* to another atom so as to complete a stable group of electrons around it. The resulting link is denoted by an arrow drawn from the atom donating the electron pair, *e.g.* in the compound formed by the addition of ammonia to boron trimethyl :

$$H_3N{\rightarrow}B(CH_3)_3,$$

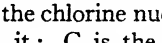
in which the 6 electrons round the boron are made up into a group of 8 by donation of the lone pair on the nitrogen. For this reason ammonia adds to many metallic salts, forming **coordination compounds**, *e.g.* $Co(NH_3)_6Cl_3$. The number of groups coordinated with the metal atom (**coordination number**) is usually 4 or 6. The atoms or groups attached to the metal (or other " central " atom) in coordination compounds are linked by covalencies and are not ionisable ; those " outside " the complex nucleus are linked by electrovalencies and are ionisable. Hence the nucleus is often enclosed in square brackets to show that it forms either a neutral molecule, as in $[Pt(NH_3)_2Cl_2]$, or a single ion :

$$[Co(NH_3)_6]Cl_3 = [Co(NH_3)_6]^{+++} + 3Cl^-.$$

Electronic formulae.—In writing electronic formulae, electrons belonging to different atoms may for clearness be represented by dots, crosses and circles, and such formulae are useful for beginners, but it must be remembered that in the resulting bonds there is no difference between the electrons and it does not matter which atom contributed any particular electron :



In electronic formulae, it must be noted, the chemical symbols stand for the so-called *atomic cores, i.e.* the nuclei plus *completed* shells of electrons other than valency electrons. Thus Cl in the formula above does not mean the chlorine atom, but the chlorine nucleus *plus* the completed neon-structure octet of electrons round it ; C is the carbon nucleus plus the completed helium structure duplet of two electrons below the outer valency electrons. No confusion need arise from this.

The **octet rule** that in covalent compounds each core is surrounded by 8 valency electrons applies only to elements of periods 2 and 3 and not to all of these, *e.g.* in SF_6 the sulphur core is surrounded by 12 valency electrons, 6 from the sulphur atom and 6 from the 6 fluorine atoms : 

The assumption that the octet is always maintained would in such cases require the linkage of some atoms by single electrons instead of by electron pairs, *i.e.* by so-called **singlet links**, *e.g.* in phosphorus pentachloride. There is no reason

why the phosphorus should not be surrounded by 10 electrons, as it is in the stable PF_5, and the existence of static singlet links is regarded as very unusual or non-occurrent.

Types of linkage.—It is seen from the preceding discussion that *two main types of linkage* are recognised :

(1) **Electrovalent** or **ionic linkage** in *ionic* (dualistic) compounds, *i.e.* salts. This is the result of a *complete transfer of electrons* from one atom to another, so as to produce two independent oppositely charged **ions**

$$:\underset{\cdot\cdot}{\overset{\cdot\cdot}{Na}}:\cdot + \cdot\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}: = [:\overset{\cdot\cdot}{\underset{\cdot\cdot}{Na}}:]^+ + [:\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}:]^-$$

Each ion forms a complete *atomic core, i.e.* its outer electron shell is the same as that of the inert gas nearest to it in the periodic system. *There is no true directed valency bond between the ions, but only non-directed electrostatic forces.* In ionic compounds the sum of the outer electrons is a multiple of 8 (*e.g.* $\overset{8}{Na}\,\overset{8}{Cl}$).

(2A) **Covalent linkage** in *non-ionic* or *covalent* (unitary) compounds. This is due to the *sharing of electrons* between two atoms, each shared pair of electrons constituting an ordinary single directed valency bond. The substance consists of neutral molecules :

$$H^{\cdot} + \cdot\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}: = H:\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}: \qquad \overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}::C::\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}} \qquad H:C:::C:H$$

(2B) A special type of covalent link is the **coordinate link,*** formed by a pair of electrons contributed by *one* atom. This may be represented either by an arrow drawn from the atom donating these electrons to the atom accepting them, as B→A, or by adding + and − signs indicating that in addition to the covalent link represented by a line there is some degree of ionic linkage due to the unequal sharing of the electron pair by the two atoms, as $B\overset{+}{—}\overset{-}{A}$. Such a link would be formed by the process $B:+A=B:A$ instead of $B^{\cdot}+\cdot A=B:A$ as in the case of an ordinary covalent bond.

An important property of a covalent (and a coordinate) link is that it has a definite direction in space, *e.g.* the single carbon bonds are directed from the atom towards the corners of a regular tetrahedron with the atom inside it, and hence these directed valency bonds may give rise to **stereoisomerism**. In covalent compounds the sum of the outer electrons is not necessarily a multiple of 8 (*e.g.* in $:\overset{\cdot\cdot}{\underset{\cdot\cdot}{F}}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{F}}:$ it is 14).

Werner's Theory

Coordination compounds.—The saturated molecules $PtCl_4$ and $2HCl$, which have no valency in the ordinary sense, combine to form a stable dibasic acid H_2PtCl_6, forming salts such as K_2PtCl_6 in which the chlorine is not ionisable

* This has received other names, *e.g. semi-polar double bond, dative bond,* and *co-ionic link* (*i.e.* intermediate between a covalent and an ionic link).

but is firmly bound to the platinum, silver nitrate giving the salt Ag_2PtCl_6. Alfred Werner in 1893 represented H_2PtCl_6 as

$$H_2[PtCl_6] = 2H^{\cdot} + [PtCl_6]'',$$

the group in square brackets being called a **nucleus**.

$PtCl_4$ also combines with $2NH_3$ to form $PtCl_4(NH_3)_2$, which does not ionise in solution and behaves as an uncharged nucleus $[PtCl_4(NH_3)_2]$. In the stable compounds formed from tervalent cobalt and ammonia, the *cobaltammines*, and in the cobaltinitrites, the cobalt atom is firmly bound to six radicals or neutral molecules, and since these are not ionisable they are supposed to be attached by covalent bonds :

$$(a) \quad [Co(NH_3)_6]Cl_3 = [Co(NH_3)_6]''' + 3Cl'.$$
$$(b) \quad [Co(NH_3)_4Cl_2]Cl = [Co(NH_3)_4Cl_2]^{\cdot} + Cl'.$$
$$(c) \quad K_3[Co(NO_2)_6] = 3K^{\cdot} + [Co(NO_2)_6]'''.$$

In (*a*) all the chlorine is ionisable, in (*b*) only one-third ; in (*c*) the nitrite radicals are bound to the metal to form a negative complex ion. The ferro- and ferricyanides contain cyanogen radicals firmly bound to iron atoms in the nuclei and give anions showing no reactions of iron or cyanides :

$$K_4[Fe(CN)_6] = 4K^{\cdot} + [Fe(CN)_6]''''$$
$$K_3[Fe(CN)_6] = 3K^{\cdot} + [Fe(CN)_6]'''.$$

In the three isomeric chromic chlorides, one, two and three chlorine atoms are ionisable, and two, one and none, respectively, are in the nucleus :

$$[Cr(H_2O)_4Cl_2]Cl + 2H_2O \quad [Cr(H_2O)_5Cl]Cl_2 + H_2O \quad [Cr(H_2O)_6]Cl_3.$$

The atoms or radicals in the nucleus are said to be **coordinated** with the central atom, and since they are not ionisable must be attached by covalencies. Their number is often six, as in the above examples, but in other series of compounds, *e.g.* of bivalent platinum, it is four, and the numbers two, three, five, seven and eight occur rather infrequently (cf. *Ann. Rep. C.S.*, 1933, **30**, 110 ; 1940, **37**, 179).

Co^{III}	Pt^{IV}
$[Co(NH_3)_6]Cl_3$ *luteo*-salts	$[Pt(NH_3)_6]Cl_4$
$\left[Co\begin{matrix}(NH_3)_5\\H_2O\end{matrix}\right]Cl_3$ *roseo*-salts	$[Pt(NH_3)_3Cl]Cl_3$
$\left[Co\begin{matrix}(NH_3)_5\\Cl\end{matrix}\right]Cl_2$ *purpureo*-salts	$[Pt(NH_3)_4Cl_2]Cl_2$ 2 forms
$\left[Co\begin{matrix}(NH_3)_4\\Cl_2\end{matrix}\right]Cl$ *praseo*-salts	$[Pt(NH_3)_3Cl_3]Cl$
$\left[Co\begin{matrix}(NH_3)_4\\(NO_2)_2\end{matrix}\right]Cl$ 2 forms : *flavo*-salts, *croceo*-salts	$[Pt(NH_3)_2Cl_4]$ 2 forms $[Pt(NH_3)Cl_3]K$
$\left[Co\begin{matrix}(NH_3)_3\\(NO_2)_3\end{matrix}\right]$ 2 forms : Gibbs's orange, Erdmann's orange	$[PtCl_6]K_2$

Co^{III}	Pt^{II}
$\left[Co\begin{matrix}(NH_3)_2\\(NO_2)_4\end{matrix}\right]K$	$[Pt(NH_3)_4]Cl_2$
	$[Pt(NH_3)_3Cl]Cl$
$\left[Co\begin{matrix}NH_3\\(BO_2)_5\end{matrix}\right]Na_2$	$[Pt(NH_3)_2Cl_2]$ 2 forms
$[Co(NO_2)_6]K_3$	$[Pt(NH_3)Cl_3]K$
	$[PtCl_4]K_2$

That the formulae give correctly the numbers of ions formed is shown by the molecular conductivities at equal concentrations :

$[Co(NH_3)_6]Cl_3$ 4 ions ; 412	$[Co(NH_3)_5NO_2]Cl_2$ 3 ions ; 240	$[Co(NH_3)_4(NO_2)_2]Cl$ 2 ions ; 97	$[Co(NH_3)_3(NO_2)_3]$ no ions ; 1·5
$[Co(NO_2)_6]K_3$ 4 ions ; 418	—	$[Co(NH_3)_2(NO_2)_4]K$ 2 ions ; 97	

The coordination number 2 is found in some compounds of ammonia with salts (*ammines*), *e.g.* $[Ni(NH_3)_2]Cl_2$ and in acid fluorides $K[HF_2]$; the coordination number 3 in $K[HgI_3]$; the number 5 is rare, *e.g.* $Fe(CO)_5$, but $Cs_3[CoCl_5]$ crystals contain the ions $Cs^{\cdot}$, $CoCl_4''$ and Cl' (Powell and Wells, *J.C.S.*, 1935, 359) ; the coordination number 7 is found in $K_2[NbF_7]$ and $K_2[TaF_7]$, and 8 in $K_4[Mo(CN)_8] + 2H_2O$ and $K_4[W(CN)_8]$.

Valency rule for coordination compounds.—An examination of the formulae given above shows that (i) *the electrovalency of the nucleus is equal to the positive valency of the metal or other central atom when this is coordinated only with saturated molecules such as* NH_3 *or* H_2O ; (ii) *if negative radicals such as* Cl, NO_2, *or* CN, *which may be regarded as ions, are in the nucleus, the positive valency of the central atom is reduced by one unit for each electrovalency of a radical present, and if the negative valency of these radicals exceeds the positive valency of the central atom, the nucleus as a whole becomes negative and is associated with a corresponding number of positive ions outside.* For example :

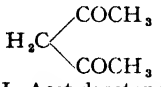
Nucleus	Valency	Compound
$[Pt^{IV}(NH_3)_4Cl_2]$	$4 - 2 = 2$	$[Pt^{IV}(NH_3)_4Cl_2]Cl_2$
$[Fe^{III}(CN)_6]$	$3 - 6 = -3$	$K_3[Fe^{III}(CN)_6]$
$[Fe^{II}(CN)_6]$	$2 - 6 = -4$	$K_4[Fe^{II}(CN)_6]$
$[Co^{III}(SO_4)(NH_3)_5]$	$3 - 2 = 1$	$[Co^{III}(SO_4)(NH_3)_5]Br$
$[Co^{III}Br(NH_3)_5]$	$3 - 1 = 2$	$[Co^{III}Br(NH_3)_5]SO_4$

The last two compounds are isomeric ; the first behaves in solution as a bromide (precipitates AgBr) and the second as a sulphate (precipitates $BaSO_4$). Positive and negative nuclei may also form salts, *e.g.* $[Cr(NH_3)_6]'''$ and $[Cr(SCN)_6]'''$ form $[Cr(NH_3)_6][Cr(SCN)_6]$. The platinous compounds $[Pt(NH_3)_4][PtCl_4]$ (green salt of Magnus) and $[Pt(NH_3)_3Cl]_2[PtCl_4]$ are of this type.

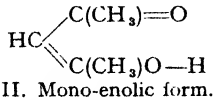
Multi-coordinating groups.—In some cases groups or radicals may occupy 2, 3 or 4 coordination positions, when they may be called *2-*, *3-* or *4-coordinating groups.*

(i) *2-coordinating* (or, formerly, " chelate ") *groups* are : ethylenediamine $NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2$, represented by en ; $\alpha\alpha'$-dipyridyl (dipy) ; radicals such as C_2O_4'', CO_3'', SO_3'', SO_4'', and the radicals of acetylacetone and dimethyl glyoxime. In the last two cases the group has one principal valency (due to loss of H from the compound) and one coordinate link is formed by the oxygen and nitrogen, respectively, by donation of a pair of electrons to the shell of the central atom to which the group is attached.

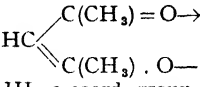
(*a*) In the case of *acetylacetone* the radical is produced from the tautomeric mono-enolic form :



I. Acetylacetone.



II. Mono-enolic form.



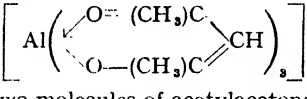
III. 2-coord. group.

Compounds of acetylacetone with elements having coordination numbers of 2, 4, 6 and 8 are known :

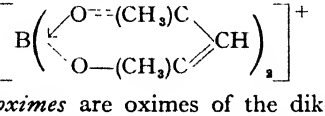
$[Na^{I}Ac]$ $[Be^{II}Ac_2]$ $[B^{III}Ac_2]\cdot X'$ $[Al^{III}Ac_3]$ $[Si^{IV}Ac_3]\cdot X'$ $[Th^{IV}Ac_4]$

Compounds similar to $[AlAc_3]$ are formed with tervalent Ga, In, Sc, Y, Ce, V, Mn, Co, and are all covalent. With boron and silicon, ions are formed.

The combination of three molecules of acetylacetone radical with an aluminium atom may be explained thus. The Al has three valency electrons which it shares with the electrons on the three lower oxygens of formula III above to form three single covalent links. The three upper oxygens form three coordinate links by donating three pairs of electrons, so that the aluminium is surrounded by a group of 12 electrons (covalency = 6) and a neutral molecule is formed :

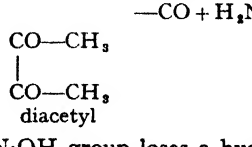


In the case of boron, two molecules of acetylacetone radical are linked to the atom, giving 2 + 4 = 6 electrons. The boron has 3 electrons, and this would make a shell of 9. The stable shell, for an element of the second period, is 8, hence one electron is lost, forming a positive ion :

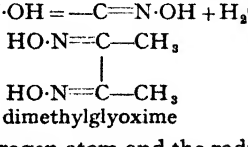


(*b*) The so-called *glyoximes* are oximes of the diketone diacetyl, formed by reaction of hydroxylamine with the two keto-groups :

$$—CO + H_2N{\cdot}OH = —C{=}N{\cdot}OH + H_2O$$

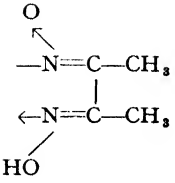


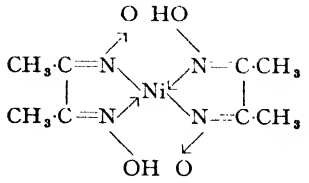
diacetyl



dimethylglyoxime

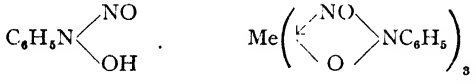
One =N·OH group loses a hydrogen atom and the radical attaches to a metal atom such as nickel by sharing an electron on the nitrogen and forming a covalent bond, whilst the other =N·OH group is attached by an electron pair on the nitrogen forming a coordinate link :



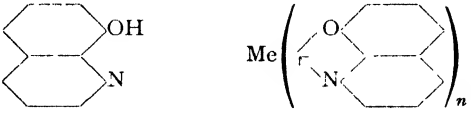


The valencies are all in a plane and *cis-trans*-isomers (p. 220) can be formed according to the orientation of the two rings (Chugaev, 1910; *Chem. Zentr.*, 1911, i, 871; Sugden, *J.C.S.*, 1932, 246; Dwyer and Mellor, *J.A.C.S.*, 1934, **56**, 1551; 1935, **57**, 605). It should be noted that the attachment is through the nitrogen, forming a 5-membered ring, not through the oxygen, as similar compounds are formed if =NOH is replaced by =NH or $=NCH_3$ (Pfeiffer, 1928, 1930).

A reagent behaving like dimethylglyoxime is *cupferron*, the ammonium salt of nitrosophenylhydroxylamine, which precipitates, *e.g.*, ferric iron:



The important reagent *oxine* is 8-hydroxyquinoline, precipitating many metals as $Me(C_9H_6ON)_n$, where n is the valency of the metal:



Many analytical reagents are of this type.

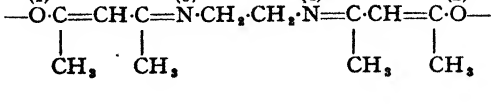
(ii) A *3-coordinating group* is $\alpha\beta\gamma$-triaminopropane (=tp):

$$NH_2{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CH_2{\cdot}NH_2,$$

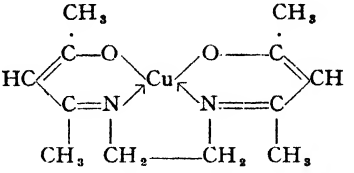
which forms compounds, by donation from the three nitrogens, with Co^{III}, Rh^{III}, etc. (Pope and Mann, *J.C.S.*, 1926, 2675, 2681; 1927, 1224): $[Co\,tp_2]Cl_3$, $[Rh\,tp_2]Cl_3$, in which tp_2 occupy six coordination positions.

(iii) A *4-coordinating group* is the enolic radical of ethylene diaminobisacetylacetone (=ec), formed by condensing two molecules of the enolic form of acetylacetone with a molecule of ethylenediamine:

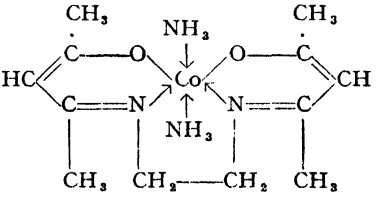
and loss of two hydroxyl hydrogens:



This attaches at (1) and (2) by electron-sharing to form ordinary covalencies and at (3) and (4) by electron donation to form coordinate links. The very stable cupric compound (Cu^{II} ec] :



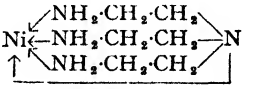
was prepared by Combes (1889). The cobaltic compound (Morgan and Smith, *J.C.S.*, 1925, **127**, 2030) can add $2NH_3$ to complete the coordination number 6 in [Co ec$(NH_3)_2$]' :



Another 4-coordinating group is $\beta\beta'\beta''$-triaminotriethylamine

$$N(CH_2{\cdot}CH_2{\cdot}NH_2)_3$$

(= tren), forming [Ni tren]SO_4, [Pt^{II} tren]I_2 (Mann, *J.C.S.*, 1926, 482 ; 1929, 409) with a tetrahedral arrangement of valencies :



Coordination and valency.—Coordination often increases the stability of compounds in a marked degree. Whereas tervalent cobalt is unstable in its simple compounds, the cobaltammines are very stable substances. Cuprous nitrate forms a stable compound with methyl cyanide, [$Cu^{I}(CH_3CN)_4$]NO_3. Cupric iodide forms stable coordination compounds such as [$Cu^{II}(NH_3)_6$]I_2. Coordination compounds of bivalent silver, [Ag^{II}(dipy)$_2$]X_2 (dipy = $\alpha\alpha'$-dipyridyl), are paramagnetic, the molecular mass-susceptibility being equal to that of bivalent copper, showing that an electron has been extracted from an inner level of the silver atom (p. 350).

Electronic theory of coordination.—Coordinate links, which behave as normal covalencies, are formed by the donation of a pair of electrons by an atom possessing a lone pair, such as nitrogen and oxygen, in the addenda (NH_3, H_2O, etc.), each bond so formed introducing two electrons to the shell of the central atom but not altering the electric charge, since the added molecule is neutral.

Electrovalencies are produced by such processes as the following: from $[Pt(NH_3)_2Cl_4]$, a neutral complex in which the atoms and groups are united by covalencies, let one Cl be removed as an *ion*, taking one electron from the shell of the metal to form $:\dot{\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}}:$ and leaving a positive charge on the metal. The *pair* of electrons so lost is then supplied by donation from a neutral NH_3 molecule added:

$$[Cl_3(NH_3)_2Pt \overset{\times}{:}\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}:] \quad [Cl_3(NH_3)_2Pt]^+ + \overset{\times}{:}\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}: \quad [Cl_3(NH_3)_2Pt : NH_3]^+.$$

A distinction is sometimes made between the *coordination number* and the *covalency* of the central atom. These are equal only when all the covalencies are single and there are no electrostatic links, but when double or triple bonds occur between the central atom and atoms or groups attached to it, the coordination number is less than the covalency.

Isomerism of complex compounds.—Several types of isomerism are predicted by Werner's theory:

(1) *Structural isomerism in the nucleus, e.g.*:

$$\left[\begin{matrix}NO—O\\NO—O\end{matrix}\right]Co\ en_2 \quad \text{and} \quad \left[\begin{matrix}O_2N\\O_2N\end{matrix}\right]Co\ en_2.$$

(2) *Ionisation isomerism*, in which positions inside and outside the nucleus are interchanged, *e.g.*

$$[Co(SO_4)(NH_3)_5]Br \text{ and } [CoBr(NH_3)_5]SO_4.$$

(3) *Coordination isomerism*, depending on the different arrangements of groups in two nuclei in combination:

$$[Cr(NH_3)_6]\cdot[Cr(SCN)_6] \text{ and } [Cr(NH_3)_4(SCN)_2]\cdot[Cr(NH_3)_2(SCN)_4].$$

(4) *Coordination polymerism*:

$$[Cr(NH_3)_3(SCN)_3] \text{ and } [Cr(NH_3)_5(SCN)]_3\cdot[Cr(SCN)_6]_2.$$

(5) *Hydration isomerism*: the groups NH_3, Cl, etc., in the nucleus may be replaced by water, H_2O, forming *aquo-compounds*:

$$[Cr(NH_3)_6]Cl_3 \rightarrow [Cr(H_2O)(NH_3)_5]Cl_3 \rightarrow [Cr(H_2O)_6]Cl_3$$
ammine compound. *aquo-compound.*

In such compounds, part of the ionisable Cl may pass into the nucleus and then ceases to be ionisable:

$$[Cr(H_2O)(NH_3)_5]Cl_3 = [CrCl(NH_3)_5]Cl_2 + H_2O.$$

The two green chromic chlorides (p. 214) are isomeric compounds of this type:

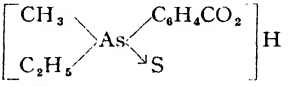
$$[CrCl(OH_2)_5]Cl_2 + H_2O \text{ and } [CrCl_2(OH_2)_4]Cl + 2H_2O.$$

The blue modification is $[Cr(OH_2)_6]Cl_3$.

(6) *Geometrical isomerism*, due to the different arrangement of the atoms and groups in space about the central metal atom.

(*a*) *Coordination number* 4. Two cases are possible :

(i) *Tetrahedral* arrangement of valencies. This is found with 4-covalent compounds of some bivalent metals, *e.g.* zinc, $[Pt(CH_3)_3Cl]$, $CoCl_4''$ in Cs_3CoCl_5 and the optically active arsenic compound :

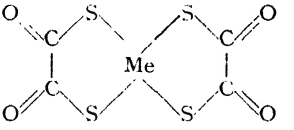


A tetrahedral configuration is found in simple ions XO_4 :

$$ClO_4' \quad MnO_4' \quad SO_4'' \quad PO_4''' \quad SiO_4'''', \text{ etc.}$$

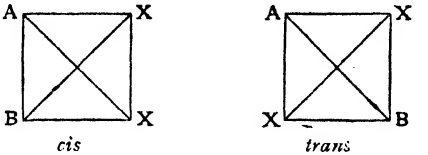
and in many simple covalent compounds of carbon, silicon, etc.

(ii) *Planar* arrangement of valencies. This is found in a number of cases. X-ray examination proves it for the compounds $K_2[PtCl_4]$, $K_2[PdCl_4]$, $[Pd^{II}en_2Cl_2]$, $[Co\,py_2\,Cl_2]$, $[Pt^{II}(NH_3)_4]\,[PtCl_4]$, $[Pd^{II}(NH_3)_4]\,[Pd^{II}Cl_4]$, $[Pt^{II}(NH_3)_4]\,Cl_2 + H_2O$, Cu^{II} with acetylacetone, benzoylacetone, etc., thio-oxalates of Ni, Pt^{II}, Pd^{II} :



and 4-covalent Cu^{I}, Ag^{I} and Au^{I} compounds.

When four groups, two of which, X, are identical, are arranged about an atom in a plane square, two geometrical isomers are possible, a *cis*-isomer when the X-groups are adjacent, and a *trans*-isomer when they are opposite :

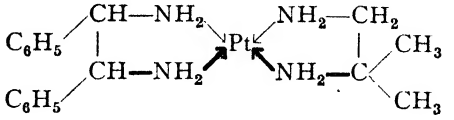


The isolation of *cis-trans* isomers proves the planar arrangement in the glyoximes (p. 216), $[Pd(NO_2)_2(NH_3)_2]$ and Pt^{II} and Pd^{II} compounds with glycine :

The magnetic susceptibility confirms the plane configuration with Pd compounds.

The plane arrangement of valencies was established for bivalent (4-covalent) platinum and palladium by optical activity. In the diphenyl-dimethyl compounds the molecule is dissymmetric and optically active (as was

found) when the platinum valencies are in one plane, as shown (the plane of the rings is at right angles to the plane of the paper, the thick lines being above this plane) (Mills and Quibell, *J.C.S.*, 1935, 839):



With a tetrahedral arrangement of valencies the molecule would have a plane of symmetry and would not be optically active.

(*b*) *Coordination number* 6. Nuclei of the type $[MeR_4X_2]$ can exist in two forms, which are represented by placing the metal atom (Me) at the centre of a regular octahedron with six covalencies directed to the six corners (Fig. 114).

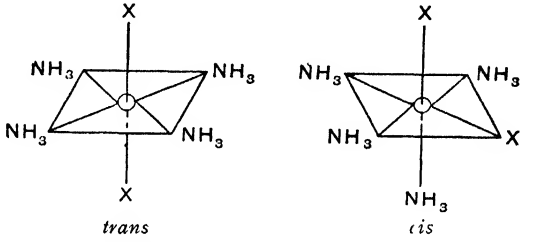
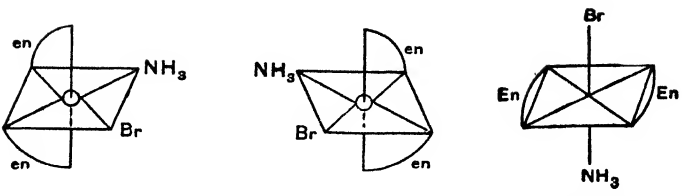


FIG. 114.—*Cis-trans* isomerism in octahedral configuration.

(The possibility that the atoms are arranged in a plane hexagon is excluded because this would lead to *three* possible isomers, whereas only two are known.) The two (univalent) nuclei of the compounds $[Co(NH_3)_4X_2]X$ are of this type. The *cis*-modifications are distinguished from the *trans*-modifications by their capacity for ring-formation.

The space figure about an 8-covalent atom in $Mo(CN)_8$ is not a cube but a duodecahedron with 8 vertices and triangular faces (Hoard and Nordsieck, *J.A.C.S.*, 1939, **61**, 2853). The octahedral arrangement of atoms or groups about the central atom in compounds such as: I. $(NH_4)_2[PtCl_6]$ and II. $[Ni(NH_3)_6]Cl_2$, has been confirmed by X-ray analysis. In I the structure of the lattice is the same as that of fluorspar with the Ca ions replaced by $PtCl_6$ and F by NH_4. In II the NH_3 molecules are arranged about the Ni in the same way as the Cl atoms in $PtCl_6$ in I and the two compounds are isomorphous.

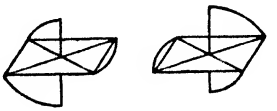
A convincing argument in favour of Werner's theory is the existence of *optical isomers*. These arise when two compounds have such arrangements of the atoms or groups in space about the central atom that one structure is the mirror-image of the other (*enantiomorphism*). The compounds shown in Fig. 115 are two optically active *cis*-forms (the metal atom is in the centre of the square), and there is also one optically inactive *trans*-form, shown on the right. The bivalent ethylenediamine group en in the *cis*-forms engages *two* valencies of the metal atom, one axial and one in the plane.



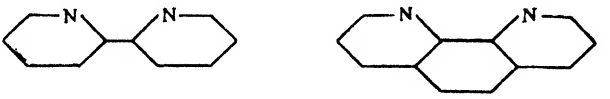
cis *trans*

FIG. 115.—Optical activity due to enantiomorphism in octahedral *cis*-configuration.

Instead of ethylenediamine many other 2-coordinating groups can give rise to optical isomerism, *e.g.* the oxalate radical C_2O_4'' in the ferrioxalates (Thomas, *J.C.S.*, 1921, **119**, 1140) $K_3[Fe(C_2O_4)_3]$, and similar compounds with tervalent Al, Cr, Co, Ru, Rh, Ir :



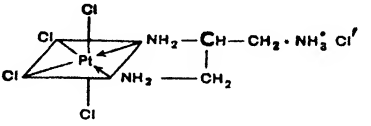
also $\alpha\alpha'$-dipyridyl (I), α-phenanthroline (II), etc.,



I II

The dipyridyl compounds (Blau, 1898; Morgan and Burstall, *J.C.S.*, 1930, 2594; Burstall, *J.C.S.*, 1936, 173) with bivalent Cu, Fe, Ni, Pt and Ru are resolvable into optical isomers.

A case in which optical activity is due entirely to coordination is the compound formed by the action of $PtCl_4$ on $\alpha\beta\gamma$-triaminopropane hydrochloride (Mann, *J.C.S.*, 1937, 1224) :



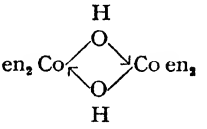
in which the carbon atom shown in black type is asymmetric.

An interesting case of high optical activity in a compound free from carbon (Werner, 1914) is that in which the univalent *positive* group containing tervalent cobalt $(HO)_2Co(NH_3)_4$ is coordinated with tervalent cobalt in the compound :

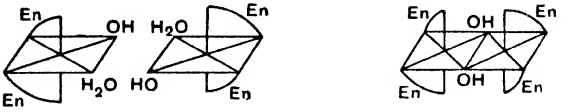
$$[Co\{\overleftarrow{}Co(OH)_2(NH_3)_4\}_3]Br_6 + 2H_2O.$$

Cases in which the positive charge of a nucleus is raised by the introduction of a positive ion are very rare : usually an increased positive charge arises from expulsion of negative ions by neutral groups.

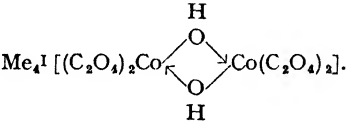
In some cases a nucleus can contain two (or more) central atoms, as in the compound :



formed by loss of water from two molecules :



and in the cobaltioxalates (Percival and Wardlaw, *J.C.S.*, 1929, 1317) :



(See on all the above *Ann. Rep. C.S.*, 1936, **33**, 157 ; 1938, **35**, 160 ; Mellor, *Chem. Rev.*, 1943, **33**, 137.)

CHAPTER IX

THE SOLID STATE

Atomic Heats

Dulong and Petit's law.—In a solid the atoms or molecules are supposed to perform small oscillations of frequency ν about fixed centres. If they execute simple harmonic motions, the sum of the kinetic and potential energies is constant; at the extreme amplitude the energy is all potential, and when the particle is passing the centre of oscillation it is all kinetic. For a large number of particles the *average* kinetic and potential energies are equal, and a calculation made by Boltzmann (1871), based on the kinetic theory, shows that the atomic heat (sp. ht. × atomic wt.) of a monatomic solid should be about 6 g. cal.

If a monatomic solid such as silver is in a vessel with a monatomic gas such as helium, the gas molecules bombard the atoms of solid and there is an exchange of energy. If the *law of equipartition of kinetic energy* (p. 34) applies, the average kinetic energies of the atoms of solid and gas are equal. At a temperature T the kinetic energy of 1 mol of monatomic *gas* is $\frac{3}{2}RT$ (p. 29), hence the average *total* energy (kinetic + potential) per mol of monatomic *solid* is $\frac{6}{2}RT$. The *atomic heat* of the solid is thus $\frac{6}{2}R = 3 \times 2 = 6$ g. cal.

This is nearly the value required by **Dulong and Petit's law** (p. 22), and at moderate temperatures (20°–100° C.) many solid elements obey the law approximately, as is seen from the table. There is an even closer agreement with the theoretical value if the atomic heats at constant volume (Ac_v) are used instead of those at constant pressure (Ac_p), which are given in the table (Lewis, *J.A.C.S.*, 1907, **29**, 1165).

Element	Atomic weight	Specific heat	Atomic heat
Aluminium	26·97	0·2240	6·04
Arsenic	74·91	0·0827	6·20
Bismuth	209·0	0·0303	6·33
Bromine (solid)	79·92	0·0705	5·63
Calcium	40·08	0·149	5·97
Chromium	52·01	0·1216	6·32
Cobalt	58·94	0·1030	6·03
Copper	63·57	0·0928	5·90
Gold	197·2	0·0316	6·23
Iodine	126·92	0·0524	6·64
Iron	55·84	0·1096	6·12
Lead	207·2	0·0309	6·41
Lithium	6·94	0·94	6·52

Element	Atomic weight	Specific heat	Atomic heat
Magnesium	24·32	0·2492	6·06
Mercury (solid)	200·6	0·0335	6·72
Nickel	58·69	0·1084	6·36
Phosphorus (white)	30·98	0·1981	6·14
Platinum	195·2	0·0320	6·25
Silver	107·88	0·0560	6·04
Sulphur	32·06	0·1751	5·61
Tin	118·7	0·0556	6·62
Uranium	238·1	0·0280	6·67
Zinc	65·38	0·0944	6·17

In many cases, especially metals, the value 6·4 gives better results than 6·3 for the atomic heat.

Exceptions to Dulong and Petit's law.—Elements of *low atomic weight and high melting point* have atomic heats lower than 6·3. Thus, although sodium (m.p. 97·6°) conforms to the law, beryllium (m.p. 1280°), boron (m.p. over 2000°), carbon (m.p. over 3500°) and silicon (m.p. 1420°), with atomic weights lower than 30, have atomic heats markedly below 6·3.

Weber in 1875 found that the specific heats of boron, carbon, and silicon increase rapidly with temperature, and the same result was found for beryllium by Humpidge in 1885. At high temperatures, the atomic heats approach 6·3.

Diamond		Graphite		Boron		Silicon		Beryllium	
°C.	At. ht.	°C.	At. ht.	°C.	At. ht.	°C.	At. ht.	°C.	At. ht.
−50	0·76	−50	1·37	−40	2·11	−40	3·81	0	3·42
10·7	1·35	10·8	1·92	26·6	2·62	21·6	4·75	100	4·28
58·3	1·84	61·3	2·39	76·7	3·01	86	5·32	200	4·93
140	2·66	201·6	3·56	177·2	3·63	184·3	5·63	300	5·38
247	3·63	249·3	3·90	233·2	4·33	232·4	5·68	400	5·61
615	5·33	640	5·40	—		—		500	5·65
808	5·44	832	5·42	—		—		—	
980	5·47	980	5·63	—		—		—	

The atomic heats of some other elements increase with temperature and may exceed 6·3 at higher temperatures. The atomic heat of lithium at −50°, 0°, 100° and 190° is 4·83, 5·22, 7·22 and 9·54 respectively.

Atomic heats at low temperatures.—The fact that abnormal atomic heats increase and approach the normal value as the temperature rises, suggests that the atomic heats of *all* elements might be abnormally small at low temperatures. This is found to be the case, as the table below shows. The atomic heats are small at low temperatures, some falling more than others, and at the absolute zero (−273° C.) they would all probably be zero.

	+20° to 100°	−188° to +20°	−253° to −195°
Carbon	2·4	1·15	0·03
Aluminium	5·9	4·73	1·12
Silicon	5·2	3·34	0·77
Iron	6·4	4·80	0·98
Copper	6·0	5·01	1·56
Zinc	6·1	5·53	2·52
Silver	6·1	5·51	2·62
Lead	6·4	6·21	4·96

The atomic heat of diamond is zero below −230° :

Temperature °C.	896	85	−41	−64	−181	−231	−243
Atomic heat	5·45	2·12	0·86	0·66	0·03	0·00	0·00

The dependence of atomic heat on temperature (abs.) is shown for a few elements in Fig. 116, from the experiments of Nernst.

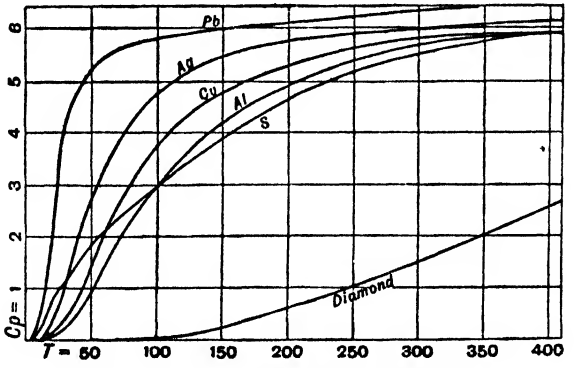


FIG. 116.—Atomic heats at low temperatures.

The quantum theory.—The rapid fall of the specific heats of solids at low temperatures, and the convergence to zero near the absolute zero, show that the energies of the atoms in a solid do not agree with the classical theory of equipartition of energy (which predicts a constant value given by Dulong and Petit's law) except at higher temperatures. A similar discrepancy was found between the law of equipartition and the variation of intensity of black-body *radiation* with temperature. In this case Planck in 1900 obtained the correct formula by introducing the **quantum theory of radiation**, which postulates that the energy of radiation cannot vary continuously, but only in whole multiples of an **energy quantum** ϵ proportional to the frequency ν: $\epsilon = h\nu$, where **h** is a universal constant, **Planck's constant**, $6{\cdot}6 \times 10^{-27}$ erg sec. This theory was then applied by Einstein in 1907 to calculate the energy of a monatomic solid.

According to the **quantum theory of specific heats**, the atoms of a solid do not take up heat continuously, but in finite quanta. The quantum ϵ varies from

element to element and is equal to $h\nu$, where ν is the **atomic frequency**, characteristic of each element. In the case of sodium, for example, $\epsilon = h\nu = 1{\cdot}9 \times 10^{-14}$ ergs.

Dulong and Petit's law is a limiting case of a general law giving the atomic heat of a monatomic solid element:

$$\text{Atomic heat} = C_v = 3R \frac{x^2 e^x}{(e^x - 1)^2}, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

where $x = h\nu/kT$, h being Planck's constant and k Boltzmann's constant, or the gas constant per *molecule*: $h/k = 4{\cdot}8 \times 10^{-11}$.

It follows from (1) that when ν (and therefore x) is very small and T is not too small, $e^x \to 1 + x$, hence $x^2 e^x/(e^x - 1)^2 \to 1$, or the atomic heat is $3R = 5{\cdot}96$, as required by Dulong and Petit's law.

The increase of C_v above $3R$ at *high* temperatures is due to the departure from simple harmonic vibration for large amplitudes, and theory shows that in such a case $C_v = 3R + CT$ ($C > 0$). Thus the curves when extrapolated to $T = 0$ should give the value $3R = 5{\cdot}96$. This has been confirmed for platinum and copper.

When the quantum is large there is less energy absorbed than when it is small and the atomic heat is abnormally low. In Figs. 117 and 118 the

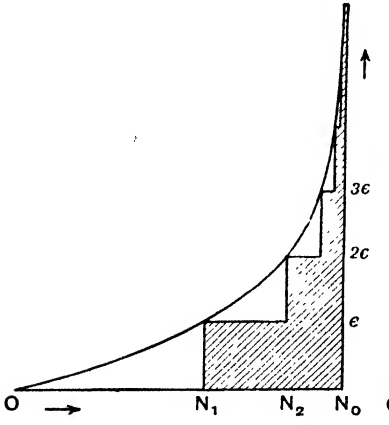


FIG. 117.—Energy distribution among aluminium atoms at 300° abs.

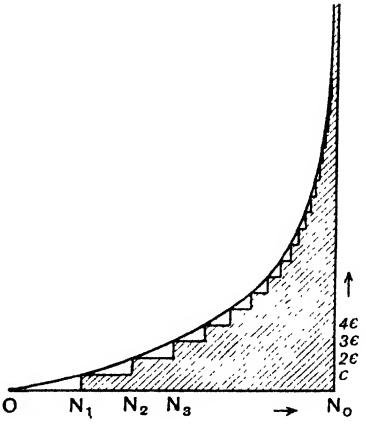


FIG. 118.—Energy distribution among lead atoms at 300° abs.

ordinates give the number of quanta absorbed and the abscissae, in which N_1 atoms out of a total of N_0 have no energy, $N_2 - N_1$ have one quantum (ϵ), $N_3 - N_2$ have two quanta (2ϵ), etc., are such that the area under the curve is proportional to the energy content. The continuous curve represents the result for continuous absorption (total area $= 3RT$; Dulong and Petit's law). The shaded area (quantum absorption) is only a small fraction of this when the quantum is large (aluminium), but very nearly this area when the quantum is small (lead).

The atomic heats at very low temperatures calculated by Einstein's equation (1) are too small. Debye in 1912 modified the theory by assuming that the atoms do not vibrate with a single frequency ν, but have a range of frequencies up to a maximum frequency ν_m, characteristic of each element. At low tem-

peratures the atomic heat is then proportional to the cube of the absolute temperature :

$$C_v = \frac{12\pi^4 R}{5}\left(\frac{T}{\theta}\right)^3 \quad \text{.....................................(2)}$$

where $\theta = h\nu_m/k$ is a *characteristic temperature.* This gives very good results, as is seen from Fig. 119, the curve representing the calculated values.

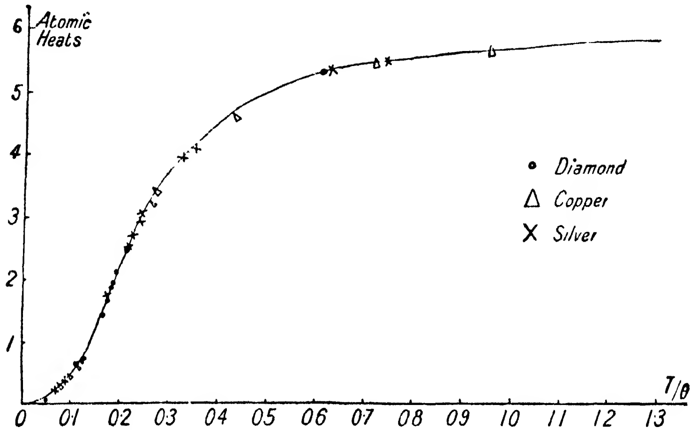


FIG. 119.—Atomic heats from Debye's equation.
Reproduced from Partington's "Chemical Thermodynamics" (Constable).

Molecular heat of a compound.—An extension of Dulong and Petit's law by F. Neumann (1831) states that *the specific heats of solid compounds of similar composition are inversely proportional to the molecular weights* :

	Mol. wt.	Sp. heat	Mol. heat
$CaCO_3$ - -	100	0·2044	20·44
$MgCO_3$ -	84	0·2270	19·1
$FeCO_3$ - -	116	0·1819	21·1
$ZnCO_3$ - -	125	0·1712	21·4
$BaCO_3$ - -	196	0·108	21·1
$PbCO_3$ - -	266	0·081	21·6

The **molecular heat** is the specific heat multiplied by the molecular weight, and Neumann's law shows that the molecular heats of *similar* compounds are equal. The relation between Neumann's and Dulong and Petit's laws was pointed out by Joule in 1844. **Joule's law** (often called Woestyn's law) states that *the molecular heat of a solid compound is the sum of the atomic heats of its constituents.* This was confirmed by Kopp (1865) and indicates that the atomic heat of an element in a solid is unchanged by combination. The heat content of a solid resides in its *atoms.* With gases, the kinetic energy of the *molecule* is predominant. Joule's law also gives the atomic heats of elements in the solid state where these cannot be directly determined.

The molecular heat of lead iodide is the sum of the atomic heat of lead and twice the atomic heat of the halogen: $6{\cdot}41 + 2 \times 6{\cdot}64 = 19{\cdot}69$. The observed value is $461 \times 0{\cdot}0427$ (sp. ht. of PbI_2) $= 19{\cdot}68$.

Sp. ht. of AgCl $= 0{\cdot}091$. $\therefore$ mol. ht. $= 0{\cdot}091 \times 143{\cdot}5 = 13{\cdot}01$. Subtracting the atomic heat of silver 6·04 gives 6·97 for the atomic heat of solid chlorine. From the molecular heats of solid compounds Kopp calculated the following atomic heats of solid elements:

Carbon	1·8	Oxygen	4·0
Boron	2·7	Sulphur	5·4
Silicon	3·8	Phosphorus	5·4

These agree with values determined for solids (except oxygen) at 0°–100°, including the abnormal values.

Crystallography

Crystal symmetry.—Solids are either *amorphous* or *crystalline*. Crystals are bodies bounded by surfaces, usually plane, arranged on a definite plan. The crystal faces meet in definite angles and the **law of constant interfacial angles** (Nicolas Steno, 1669) asserts that *the crystal angles are constant for all crystals of a substance of the same form*. The interfacial angles in the ideal octahedral alum crystal and in the imperfect crystal (Fig. 120), in which certain faces have developed more than others, are identical. On some crystals there are two or more sets of faces belonging to different forms of the same crystal system, *e.g.* the galena crystal in Fig. 121 is a cube with octahedral faces at the corners.

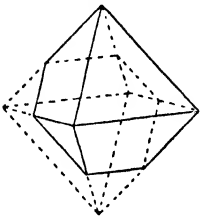


FIG. 120.—Ideal and imperfect octahedra, showing constancy of angles between the faces.

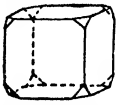


FIG. 121.—Combination of cube and octahedron.

Crystals possess definite elements of symmetry, except in one class, which has none. A **plane of symmetry** in a crystal divides it into two halves each the mirror image of the other, and if a crystal is rotated around an n-fold **axis of symmetry** it occupies the same position in space n times in a complete turn (360°). A crystal has a **centre of symmetry** when like faces are arranged in pairs in corresponding positions on opposite sides of a central point.

A cube has 9 planes of symmetry (shown in Fig. 122), a centre of symmetry, and 13 axes of symmetry, of which three (passing through centres of opposite faces) are axes of 4-fold symmetry, four (the diagonals) are axes of 3-fold symmetry (*trigonal axes*), and six (through the centres of diagonally opposite edges) are axes of 2-fold symmetry (*digonal axes*). The cube has therefore 23 elements of symmetry, the highest number possible in a crystal.

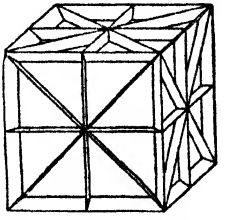


FIG. 122.—Planes of symmetry of a cube.

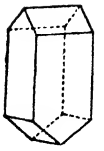
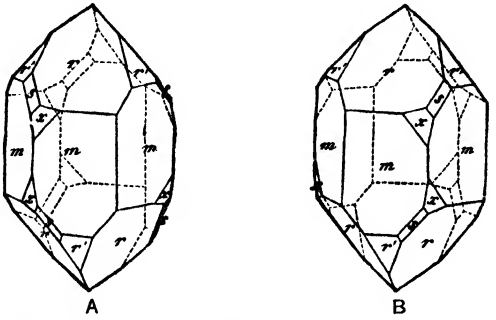


FIG. 123.—Epsom salt crystal.

Some crystals have no plane of symmetry, others have no axes of symmetry, others have no centre of symmetry, and some have no elements of symmetry at all.

The crystal in Fig. 123 seems to have an axis of 2-fold symmetry, but if the upper front sloping face is rotated through 90° and then reflected in a horizontal plane we obtain the lower right-hand sloping face as a virtual image, and the crystal is said to have an *alternating axis* of 4-fold symmetry. A *polar axis* has different groupings of faces about its two ends; the enantiomorphous quartz crystals in Fig. 124 have polar axes.



A B

FIG. 124.—Enantiomorphous crystals of quartz; A left-handed, B right-handed, crystal. The dissymmetry is produced by the small faces *s* and *x*, which on the two crystals are in the relation of mirror-images.

By arranging the elements of symmetry and adding the one case where there are no elements of symmetry, it is found that there are 32 **symmetry groups**, of which 11 include nearly all the common crystal forms. A simpler arrangement is into the six so-called **crystallographic systems.**

Crystallographic systems.—The position of any crystal face is defined by its intercepts on three or more *crystal axes* intersecting in a point. These axes (which are not necessarily axes of symmetry) may be of *six types*:

(1) *Three equal axes at right angles*: the **cubic** or **regular system** (*a a a*), of which the cube is the typical *prism form* and the regular octahedron the typical *pyramid form* (Fig. 125, I).

(2) *Two equal axes at right angles and a third longer or shorter axis meeting these at right angles*: the **tetragonal system** (Fig. 125, II) (*a a c*).

If the length of the vertical axis is *c* and the lengths of the horizontal axes *a* and *b*, the cubic system may be denoted by (*a a a*) and the tetragonal system by (*a a c*).

(3) *Four axes, three equal and intersecting in a plane at angles of* 60°, *and one longer or shorter axis at right angles* (Fig. 125, III): the **hexagonal system** (*a a a c*).

(4) *Three unequal axes at right angles* (Fig. 125, IV): the **rhombic system** (*a b c*). The longer lateral axis is called the *macro-axis* and the shorter the *brachy-axis*.

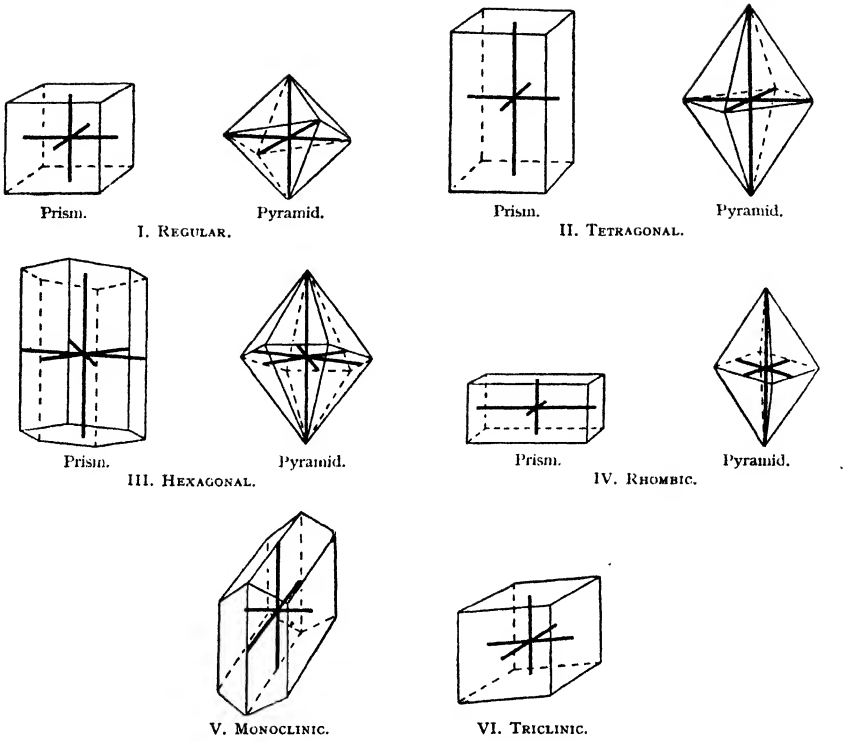


FIG. 125.—Crystallographic systems.

(5) *Three unequal axes, two intersecting at an oblique angle β and a third at right angles to these* (Fig. 125, V) : the **monoclinic system** (*a b c*).

(6) *Three unequal axes intersecting obliquely at angles α, β, γ* (Fig. 125, VI) : the **triclinic system** (*a b c*).

Sometimes the rhombohedron (Fig. 130) is put into a separate system, making 7 in all; it is here regarded as a hemihedral form (p. 232) of the hexagonal system.

Domes and pinakoids.—Types of faces known as **domes** and **pinakoids** are met with in the rhombic and monoclinic systems. Prism faces developed parallel to one of the lateral axes and intersecting the other two axes are called **dome faces.** If parallel to the longer or macro-axis they are **macrodomes**; if parallel to the shorter or brachy-axis they are **brachydomes** (Fig. 126).

Prism faces intersecting one lateral axis and parallel to the other two axes are called **pinakoid faces**; **macropinakoids** intersect the macro-axis, **brachypina-**

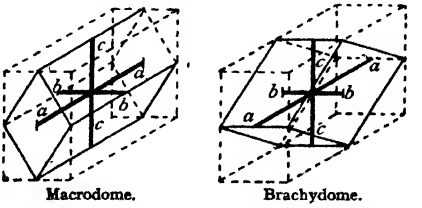


FIG. 126.—Dome and pinakoid faces in the rhombic system.

koids the brachy-axis. These are the diamond-shaped end faces in Fig. 126. In Fig. 127, representing a crystal of barytes ($BaSO_4$), the faces marked 010 constitute a macropinakoid form, in this case a **basal pinakoid**; the faces 101 are the macrodome form. The faces belonging to the prism form are marked 001, a notation explained later.

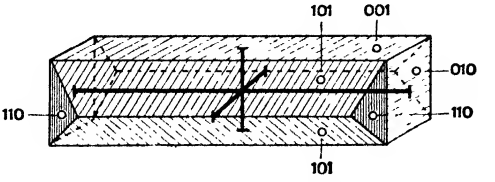


FIG. 127.—Barytes crystal.

Hemihedral and tetartohedral forms.—Those forms in any system which have the full number of faces required by the symmetry are called **holohedral forms**. If only half the number of faces occurring in the holohedral form are present, the form is known as **hemihedral**; forms exhibiting only one quarter the full number of faces are called **tetartohedral**. (In the modern classification into symmetry groups these are holohedral forms in separate classes.) A hemihedral form is produced by suppressing half the faces of the holohedral form and producing the remainder so as to meet in new edges. The tetrahedron is the hemihedral form of the octahedron (Fig. 128).

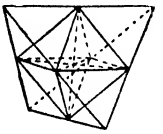


FIG. 128.—Relation of tetrahedron (hemihedral form) to octahedron (holohedral form).

By developing alternate (shaded or unshaded) faces of the hexagonal pyramid (Fig. 129), the positive or the negative **rhombohedron** (Figs. 130, 131) is produced.

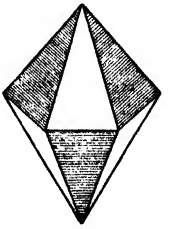


FIG. 129.
Hexagonal pyramid.

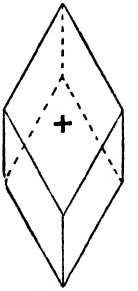


FIG. 130.
Positive rhombohedron.

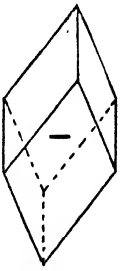


FIG. 131.
Negative rhombohedron.

From the dihexagonal pyramid with 24 faces, obtained by the combination of two hexagonal pyramids, two kinds of hemihedral forms are produced: (i) by suppressing alternate pairs of faces (Fig. 132) we obtain the **scalenohedron** (Fig. 133), and (ii) by suppressing alternate faces (Fig. 134) the **trapezohedron** (Fig. 135).

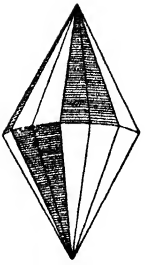


FIG. 132. Dihexagonal pyramid.

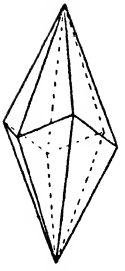


FIG. 133. Scaleno-hedron.

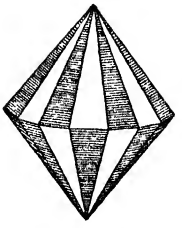


FIG. 134. Dihexagonal pyramid.

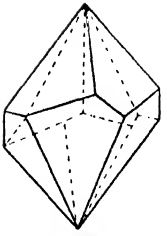
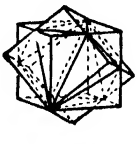


FIG. 135. Trapezo-hedron.

Twin crystals.—Two or more individual crystals which grow in contact so that neither is complete form a **twin crystal** (Fig. 136). The two crystals may coalesce except for a few faces, as in Fig. 137.



Fluorspar.

Gypsum.

FIG. 136.—Twin crystals.

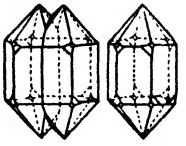


FIG. 137.—Twins of right- and left-handed quartz. Partial and complete interpenetration.

Crystallographic notation.—The form shown in Fig. 138 contains two sets of faces, the set *a*, *b*, *c* and the face *o*. Through the centre *O* axes *OX*, *OY*, *OZ* parallel to the faces are drawn as shown. These are the **crystallographic axes.** In the general case (for a triclinic crystal), they will be oblique, and the angles $YOZ = \alpha$, $XOZ = \beta$ and $XOY = \gamma$ will not be right angles. Each prism face cuts one axis only, since it is parallel to the other two, and the **intercepts** are the distances *a*, *b* and *c* from *O*. If we imagine the face *o* extended in all directions it will intercept all three axes: whatever the size of *o* its intercepts will remain in the same *ratio*. These ratios, generally denoted by $a : b : c$ for the intercepts on the *x*, *y* and *z* axes, were called by Weiss (1818) the **parametral ratios,** the face *o* being the **parametral plane.** For the other pyramid faces the ratios of the intercepts are $a : -b : c$, $a : b : -c$, and $a : -b : -c$.

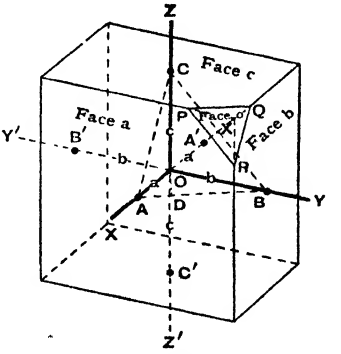


FIG. 138.—Crystallographic axes.

In *all* cases (whether the axes are rectangular or inclined), if *o* is an actual crystal face the intercepts of *any other* actual face of the crystal can be expressed by the ratio $ma : nb : oc$, where *m*, *n*, *o* are either small *whole* numbers or infinity. For example, the prism face *b* makes intercepts $\infty a : 1b : \infty c$, since it

is parallel to OX and OZ and its intercepts are infinite, whilst it cuts OY at a point B which may also be taken as the intercept of a face parallel to o.

This **law of rational intercepts** was implied in the attempts of Haüy since 1781 (*Essai d'une Théorie sur la Structure des Crystaux*, 1784), to produce derived forms by the decrements of successive layers of what he called *integrant molecules*, the form of which is that of the cleavage figure. The forms of rock-salt, for example, are produced by packing the hypothetical cubic integrant molecules together, and the development of an octahedral face ABC is shown in Fig. 139.

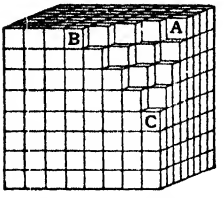


FIG. 139.—Integrant molecules according to Haüy.

In the usual or **Miller system** of crystallographic notation (1839), the axial ratios $a : b : c$ are first calculated from the interfacial angles as measured by a goniometer; the intercepts $\infty a : 1b : \infty c$, for example, are then written $\frac{a}{\infty} : \frac{b}{1} : \frac{c}{\infty}$, and the denominators enclosed in a bracket are the **Miller indices** of the face, (010) for the face b, and (111) for the face o. In the case of negative indices the sign is placed over the index ($1\bar{1}1$).

As an example, consider the triclinic potassium dichromate crystal in Fig. 140. The edges selected for the directions of the three crystallographic axes OX, OY, OZ are the intersections of the faces B and C, C and A, and A and B, respectively. Hence the faces A, B and C will have the indices (100), (010) and (001) respectively. The parametral face chosen, giving the basic ratio $a : b : c$, is p, and since it cuts the axis OZ at its negative end, its indices will be ($11\bar{1}$). The ratios $a : b : c$ and the angles α, β, γ between the axes ($\alpha = YOZ$; $\beta = XOZ$; $\gamma = XOY$) are calculated from the different angles which these four faces A, B, C and p, make with one another, as found by a goniometer. They are $a : b : c = 1{\cdot}0116 : 1 : 1{\cdot}8416$; $\alpha = 98° 0'$; $\beta = 96° 13'$; $\gamma = 90° 51'$. (It is customary to put the b axis ratio = 1.) The indices of the remaining faces are then found to be (as lettered in the figure): $s(10\bar{1})$, $r(101)$, $m(110)$, $n(1\bar{1}0)$, $q(01\bar{1})$, $t(012)$, $o(1\bar{1}1)$, obeying the law of rational intercepts.

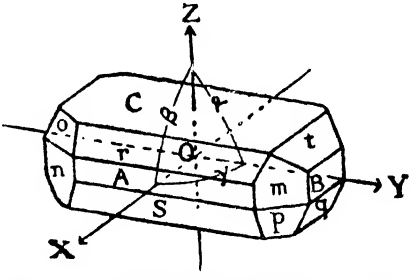


FIG. 140.—Potassium dichromate crystal.

Space lattices.—Bravais in 1848 replaced the idea of a packing of integrant molecules by an open structure in which the ultimate particles, which are considered as spheres, are arranged in a **lattice** (Fig. 141), of which he recognised 14 types. By considering the grouping of points, representing the centres of atoms, in space lattices it has been shown that there are 230 generalised types, such that the assemblage around any selected point is the same as, or the mirror-image of, the assemblage around any other point in the lattice. These 230 types may be allocated to classes according to symmetry. Some examples of space lattices are considered later (p. 240).

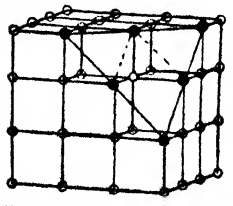


FIG. 141.—Space lattice of sodium chloride.

Isomorphism

Haüy (1743–1822) laid down the axioms: (i) *identity of crystalline form* (except in the regular system) *implies identity of chemical composition*; and conversely, (ii) *difference in crystalline form implies difference in chemical composition.*

Isolated cases of the same substance crystallising in different forms ($CaCO_3$ as calcite and aragonite) and different substances in the same form (the alums, etc.) were known, and in 1819 Mitscherlich (*Ann. Chim.*, 1820, **14**, 172; 1822, **19**, 350) showed that phosphates and arsenates of similar composition and containing the same amount of water of crystallisation had almost exactly the same crystalline form, or are **isomorphous**: *e.g.*

$Na_2HPO_4 + 12H_2O$, disodium hydrogen phosphate
$Na_2HAsO_4 + 12H_2O$, disodium hydrogen arsenate.

The ordinary forms of $NaH_2PO_4 + H_2O$ and $NaH_2AsO_4 + H_2O$ differ, but the phosphate sometimes crystallises in the common form of the arsenate.

Mitscherlich pointed out that the existence of octahedral and monoclinic sulphur shows that elements also may have different crystalline forms. One substance may have two crystalline forms and is **dimorphous**, or more than two forms, when it is **polymorphous.**

Mitscherlich at first thought that the same number of atoms combined in the same way produce the same crystalline form, no matter what is the chemical nature of the atoms, but he afterwards said that it is only atoms of chemically analogous elements which can replace one another without producing a change of form.

More accurate measurements of crystal angles showed, as Mitscherlich conjectured, that the law is only approximate. Wollaston (*Phil. Trans.*, 1812, 159) had found with his reflecting goniometer that the corresponding angles in calcite, dolomite, and spathic iron ore are 74° 55′, 73° 45′, and 73° 0′. Except in the regular system the replacement of one atom by an atom of an isomorphous element leads to a change in crystal angles which may be small, but may be several degrees. Haüy's first axiom is therefore correct in the strict sense.

Tutton (1893–1925) found that the crystal angles in isomorphous sulphates and selenates of potassium, rubidium, and caesium change slightly when one element (K, Rb, Cs, or S, Se) is replaced by another. The change, expressed in terms of the ratios of the lengths of the axes *a*, *b*, *c*, depends in a regular manner on the atomic weight of the element:

K_2SO_4	$a : b : c = 0{\cdot}5727 : 1 : 0{\cdot}7418$
Rb_2SO_4	$a : b : c = 0{\cdot}5723 : 1 : 0{\cdot}7485$
Cs_2SO_4	$a : b : c = 0{\cdot}5712 : 1 : 0{\cdot}7531$
$(NH_4)_2SO_4$	$a : b : c = 0{\cdot}5635 : 1 : 0{\cdot}7319$

The other properties (molecular volume, refractive indices, coefficients of expansion, thermal conductivity) alter with the crystal angles, showing that the form is closely related to the nature of the atoms in the crystal.

Isomorphous substances sometimes form **overgrowth crystals.** A violet octahedral crystal of chrome alum is covered with a colourless overgrowth of potash alum of the same form when it is suspended by a thread in a saturated solution of the potash alum, and a green crystal of nickel sulphate $NiSO_4,7H_2O$ may be covered with colourless zinc sulphate $ZnSO_4,7H_2O$. The formation of overgrowth crystals was regarded by Kopp (1879) as characteristic of isomorphous substances, but exceptions are known.

Atomic weights and isomorphism.—The application of isomorphism to the deduction of atomic weights is based on the axiom that *isomorphous compounds have similar formulae* (p. 22).

An interesting example of isomorphism, which enabled Roscoe (1867) to fix the atomic weight of vanadium, is that of the minerals :

	Berzelius	Roscoe
apatite - - -	$3Ca_3(PO_4)_2, CaF_2$	$3Ca_3(PO_4)_2, CaF_2$
pyromorphite - -	$3Pb_3(PO_4)_2, PbCl_2$	$3Pb_3(PO_4)_2, PbCl_2$
mimetite - -	$3Pb_3(AsO_4)_2, PbCl_2$	$3Pb_3(AsO_4)_2, PbCl_2$
vanadinite - -	$3Pb_3(VO_3)_2, PbCl_2$	$3Pb_3(VO_4)_2, PbCl_2$

Berzelius gave them the formulae shown, that of vanadinite differing from the others. Rammelsberg (1856), however, found that all the minerals crystallise in the same form, and Roscoe concluded that the formulae should be similar.

By reinvestigating vanadium compounds he found that what Berzelius regarded as metallic vanadium was an oxide VO, so that Berzelius's VO_3 was VO_4, and the formulae were then analogous. The atomic weight of vanadium, 68·5, found by Berzelius was the molecular weight of VO, corresponding with $V = 68·5 - 16 = 52·5$. Roscoe found that the actual vanadium compounds used by Berzelius contained phosphoric acid, which is difficult to separate, and by using pure compounds he found $V = 51·4$.

Mixed crystals.—Isomorphous substances such as potash alum $KAl(SO_4)_2, 12H_2O$ and chrome alum $KCr(SO_4)_2,12H_2O$ crystallise together in variable proportions from solutions to form homogeneous crystals called *mixed crystals* or *solid solutions*. In other cases these are formed from a fused state on cooling (p. 66).

Substances which crystallise in the same form but belong to different chemical types do not form mixed crystals, or only to a very limited extent, whereas chemically analogous compounds may form mixed crystals even though the crystal angles differ by as much as 5°, and the resulting crystal angles lie between those of the components.

Retgers (1889) considered that the variation in physical properties of mixed crystals with the proportions of the constituents is a criterion of true isomorphism. If the specific volume (1/density) is plotted against the ratio of the constituents the points must lie on a straight line which shows no changes of direction. When the substances are only partially miscible there is a gap in the line, but if they are isomorphous one part of the line is a continuation of the other.

There are many exceptions to Retgers' theory. Potassium and sodium chlorides crystallise in the same form and have identical lattices but do not form mixed crystals. The capacity for forming mixed crystals seems, in fact, to depend on approximate equality of the volumes of the structural units. Ammonium sulphate $(NH_4)_2SO_4$ with the molecular volume (M.V.) 74, mixes in all proportions with rubidium sulphate Rb_2SO_4 (M.V. 73), with potassium sulphate K_2SO_4 (M.V. 65) and caesium sulphate Cs_2SO_4 (M.V. 85), whilst potassium and caesium sulphates are completely immiscible, although they are undoubtedly isomorphous. The name *isomorphism* is best restricted to its original meaning of close similarity in crystal form.

Peculiar cases of isomorphism.—Apparent exceptions to the law of isomorphism are due in some cases to *dimorphism* or *polymorphism*, an example of which was discovered by Mitscherlich in NaH_2PO_4,H_2O and NaH_2AsO_4,H_2O. The substance exists in two or more forms, only one of which is isomorphous with the common form of the second substance.

Isomorphism is also found between *chemically similar* substances having different numbers of atoms in the molecule: ammonium salts containing NH_4 are isomorphous with potassium and sodium salts containing K and Na; and silver sulphide Ag_2S in the mineral *argentite* is isomorphous with lead sulphide in *galena* PbS, the two forming mixed crystals. In other cases compounds are isomorphous which are *not chemically analogous* but have the same numbers of atoms in the molecule: calcium carbonate $CaCO_3$ occurs in the same form (*calcite*) as sodium nitrate $NaNO_3$, and Mg_2SiO_4 and Al_2BeO_4 are isomorphous. Crystals of sodium nitrate will form parallel growths on calcite crystals.

Other examples of this type (T. V. Barker, *J.C.S.*, 1912, **101**, 2484) are:

(1) Potassium periodate KIO_4
Calcium tungstate $CaWO_4$
Potassium osmiamate $KOsO_3N$

(2) Potassium sulphate K_2SO_4
Potassium beryllium fluoride K_2BeF_4

(3) Potassium perchlorate $KClO_4$
Barium sulphate $BaSO_4$
Potassium fluoborate KBF_4

(4) Yttrium phosphate YPO_4
Zircon $ZrSiO_4$
Tinstone SnO_2 or $SnSnO_4$

In each of these groups the molecule contains the same number of atoms, and the original idea of Mitscherlich that the form depends on the number of atoms and not on their chemical nature appears to be verified.

Isomorphous alums (Curjel, *Nature*, 1929, **123**, 206) are:

$$K_2SO_4, Al_2(SO_4)_3, 24H_2O$$
$$K_2BeF_4, Al_2(SO_4)_3, 24H_2O$$
$$K_2ZnCl_4, Al_2(SO_4)_3, 24H_2O$$

and the isomorphism of $BaSO_4$ and $BaBeF_4$ has been proved by X-ray analysis (N. N. Rây, 1931–2). It will be seen (p. 248) that: (i) molecules or ion-pairs of closely similar *shape* (or, in ion-pairs, nearly equal ionic radii) usually form cells also of similar shape; (ii) molecules of similar shape and also nearly equal *volumes* give cells of similar size and shape; (iii) corresponding elements of the same periodic group (or at least of the same valency) form molecules with the same types of valency bonds.

Crystal Structure

X-rays and crystals.—For a long time it was not possible to obtain diffraction of X-rays by matter, since the wave-lengths of X-rays (below 500 A.) are much smaller than those of light (6470–4240 A.). Friedrich, Knipping, and Laue in 1912 showed that X-rays are diffracted in passing through crystals; and the work (from 1912) of W. H. Bragg and W. L. Bragg proved that they are reflected from crystal surfaces at definite angles of incidence in the same way as light from a diffraction grating (Fig. 142).

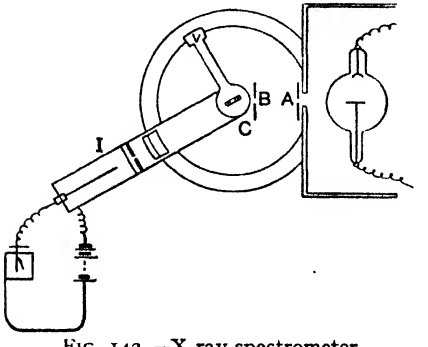


Fig. 142.—X-ray spectrometer.

The X-rays emitted at a glancing angle from the anticathode of the X-ray tube on the right pass through lead slits *A* and *B*, and the pencil of rays falls on the crystal *C*. The reflected rays pass into an ionisation chamber *I* containing a gas (*e.g.* SO_2), and the ionisation current is measured by the electroscope. The crystal and ionisation chamber are pivoted at the centre of a graduated circle and the angle of incidence θ is read by a vernier *V*. Only at certain angles are rays reflected into *I*.

If the primary X-rays are homogeneous, *i.e.* all of the same wave-length, the series of directions along which reflexion occurs are obtained by giving the values 1, 2, 3, ... to n in the general equation: $2d \sin \theta = n\lambda$, where λ is the wave-length. In the ordinary diffraction grating d is the space between the rulings; in X-ray reflexion W. L. Bragg identified d with the distance between planes in the crystal corresponding with the densest arrangement of the atoms. The rock-salt grating distance is about 3 A.; the ruling distance in a Rowland grating is about 10,000 A.

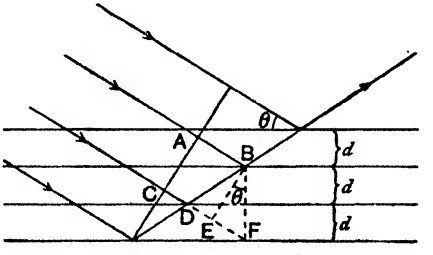


Fig. 143.—Reflexion of X-rays from a crystal.

In Fig. 143 a parallel beam of X-rays of wave-length λ is shown reflected from various planes of atoms distant d apart, θ being the angle of incidence with the crystal surface. The difference of path for two rays is:

$$CD + DB - AB = DB - DE = DF - DE = EF = 2d \sin \theta.$$

The two rays are in phase and reinforce each other when this is a whole multiple n of the wave-length λ, or $2d \sin\theta = n\lambda$. If d is known λ can be found, and conversely.

It had been suggested by crystallographers (p. 234) that the rock-salt crystal was a *lattice* of sodium and chlorine atoms. These can be regarded as spheres in contact and packed together so that the *centres* of the spheres occupy the positions shown in Fig. 144. In this the *centres* of the sodium atoms are represented by ○ and the *centres* of the chlorine atoms by ●. It is now known that these are the sodium and chlorine *ions* Na^+ and Cl^- (p. 210). If the side of the large cube in the figure is a, then the distance between the centres of two adjacent atoms is $d = a/2$. This distance d in rock-salt is taken as a standard in X-ray measurements.

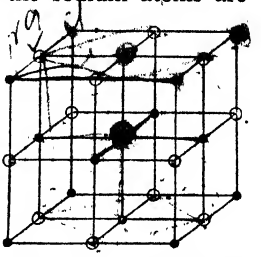


FIG. 144.—Arrangement of atoms in rock-salt lattice. ○ = Na ● = Cl.

In the large cube there are 14 chlorine ions, eight of which are at the corners. Each of these belongs to eight cubic lattices which may be packed around it, only one of these being shown as the large cube. The other six chlorine ions are on the faces, and each is common to two cubic lattices, one of which is shown as the large cube. Hence, of the 14 atoms, a single cubic lattice has a share of eight $\frac{1}{8}$ atoms, and six $\frac{1}{2}$ atoms, or $1 + 3 = 4$ atoms in all. Of the 13 sodium ions shown, one is at the centre and 12 are at positions where each is shared by four lattices (one only shown), *i.e.* in one lattice there are $1 + 3 = 4$ atoms. The volume of the lattice is $a^3 = 8d^3$, where a is the side of the lattice and $d\,(= \frac{1}{2}a)$ is the distance between the planes of atoms. Thus d^3 is associated with the mass of one-eighth of 4 sodium atoms and 4 chlorine atoms, or half a molecule of NaCl. This is $\frac{1}{2}M/\mathbf{N} = \frac{1}{2} \times 58{\cdot}5/6{\cdot}03 \times 10^{23}$ g., where M = mol. wt. and $\mathbf{N}$ = Avogadro's number. But this mass is also equal to d^3 multiplied by the density of rock-salt, 2·17, hence $\frac{1}{2} \times 58{\cdot}5/6{\cdot}03 \times 10^{23} = 2{\cdot}17 \times d^3$, or $d = 2{\cdot}82 \times 10^{-8}$ cm.

The original method of Laue, viz. the production of a diffraction pattern of spots by a beam of rays passing *through* a plate of crystal cut in a particular direction, is also used in crystal analysis.

A third method, developed independently by Debye and Scherrer and by Hull, is the *powder method*. A beam of X-rays is intensely reflected from the structural layers in a crystal only when it meets them at proper angles. A powder consists of innumerable small crystals orientated in chaotic fashion, but there will always be a number in correct orientation for the reflexion of a transmitted beam of X-rays. The powder is contained in a very thin glass tube placed parallel to the slit or in the direction of a beam transmitted through a small hole, or else the powder is spread out over a plate arranged for reflexion as in Bragg's method. When the transmission method is used the pencil of rays is spread into a series of cones, the intersections

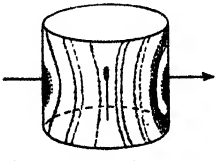


FIG. 145.—The powder method. The crystal powder is contained in the thin tube in the axis of the cylinder.

of which on a cylindrical photographic film produce a series of segments of circles arranged on each side of the central spot corresponding with the axial undeviated pencil (Fig. 145).

Cubic lattices.—The simplest lattice is the cubic, of which there are three types, viz. the **simple cubic lattice**, the **body-centred cubic lattice**, and the **face-centred cubic lattice**. The simple cubic lattice is shown as one of the eight units in Fig. 144, the body-centred cubic lattice as *A* in Fig. 146, and the face-centred cubic lattice as one of the eight units in *B* in Fig. 146. The first has eight atoms at

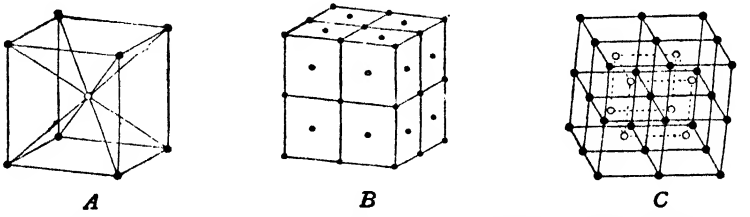


FIG. 146.—Body-centred (*A* and *C*) and face-centred (*B*) cubic lattices.

its corners, in the second there is one extra atom at the centre of the cube, and in the third there are six additional atoms at the centres of the faces of the simple cubic lattice.

The body-centred lattice may be produced by the interpenetration of two simple cubic lattices in such a way that the corners of one lattice occupy the centres of the cubes of the second as shown in *C*, Fig. 146. In each unit cell of the body-centred lattice there are $1 + 8/8 = 2$ atoms, whilst the unit cell of the simple cubic lattice contains $8/8 = 1$ atom. The unit cell of the face-centred lattice shares $\frac{1}{8}$ of each corner atom and $\frac{1}{2}$ of the atom at the centre of each of the six faces, and thus contains $8/8 + 6/2 = 4$ atoms.

The **alkali metal halides** belong to two types of cubic lattice :

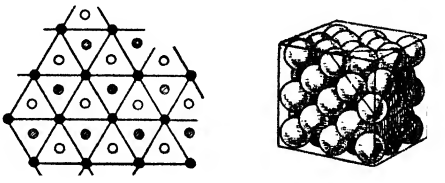
(1) CsCl, NH_4Cl and NH_4Br crystallise in *body-centred cubic lattices*. Each Cs atom is surrounded by 8 Cl atoms, but as each of the latter is shared by 8 unit cubes the unit cell contains 1Cs + 8/8Cl, or one CsCl molecule.

(2) Na, K and Rb halides and NH_4I crystallise in *simple cubic lattices*, with atoms of alkali metal and of halogen occupying alternate lattice points. Each small cube contains $4 \times \frac{1}{8} = \frac{1}{2}$ atom of each element. Each atom is surrounded by six equidistant atoms of the other kind. This *rock-salt lattice* may be formed by the interpenetration of two face-centred cubic lattices, one of metal atoms and the other of halogen atoms. Each crystallographic elementary cube (the whole figure) contains 8 cubelets, and hence 4 atoms each of metal and halogen.

It is probable that the alkali metal halides may exist in either form, depending on temperature and pressure ; this is known to be the case for ammonium halides, and CsCl changes from a body-centred to a face-centred cubic lattice above 450°.

Hexagonal lattices.—The arrangement of atoms in a face-centred cubic lattice is the *closest packing of spheres*. In a layer of equal spheres in contact there will be a triangular space between every three, and in each triangular

space another sphere may be placed to form a second layer. In Fig. 147 *a*, the centres of the lower spheres are shown as • and those in the second row as ○. A third layer of spheres may be added in two ways. Either they may be placed so as to occupy the positions shown by ⊘, when the face-centred cubic lattice is obtained, built up on the octahedral surface (Fig. 147 *b*), or they may be arranged in the positions shown by •, *i.e.* vertically above the atoms in the first layer, when a lattice with hexagonal symmetry is obtained, viz. the *hexagonal closest packing of spheres*: it consists of two interpenetrating hexagonal lattices, the first comprising the atoms in the layers 1, 3, 5, ..., and the second the atoms in the layers 2, 4, 6, ... The ratio of the axes for equal spheres is $c : a = 1{\cdot}633 : 1$.



a *b*

FIG. 147.—Close packing of spheres to form face-centred cubic and closest-packed hexagonal lattices.

Lattice structures of metals and binary compounds.—Metals crystallising in *face-centred cubic lattices* are: Ag, Al, Au, Ca-α, Ce-β, Co-β, Cu, Fe-γ, Ir, La-β, Ni-β, Pb, Pd, Pt, Rh-β, Sr, Th, Tl-β; and the inert gases (He, Ne, A, Kr, Xe) also crystallise in this form. It should be clear from Fig. 146*B* that the atom at the centre of an upper small face is surrounded by 12 atoms at the shortest distance, viz. the 4 at the corners and 8 at the centres of the vertical small faces above and below; crystallographers (using the name in a sense different from that used by chemists, p. 219) say that the *coordination number* in this lattice is 12.

Metals crystallising in *body-centred cubic lattices* are: Ba, Cr-α, Cs, Fe-α, Fe-δ, K, Li, Mo, Na, Nb, Rb, Ta, U-β, V, W-β, Zr-β. The coordination number is 8. No examples of the simple cubic lattice are known among metals.

Metals crystallising in close-packed *hexagonal lattices* are: Be, Ca-γ, Cd, Ce-α, La-α and some other rare-earth metals (p. 403), Cr-β, Co-α, Hf, Hg, Mg, Ni-α, Os, Re, Ru, Ti, Tl-α, Zn, Zr-α. The coordination number is 12. The distances between the atomic centres in the cubic and hexagonal lattices of metals vary from 2·5 to 5·5 A.

Germanium and white tin crystallise in *tetragonal lattices*; arsenic, antimony and bismuth in *trigonal lattices* (which may be regarded as sheared elongated cubes); manganese crystallises in three modifications of unusual structure. Gallium is rhombic (not tetragonal) and the solid contains Ga_2 molecules.

Most **binary compounds** AB crystallise in cubic or hexagonal lattices:

(1) *Body-centred cubic lattices*: CsCl, CsBr, CsI, RbF, TlCl, TlBr, TlI, NH_4Cl, NH_4Br, CuZn, AgZn, AuZn, AlNi.

(2) *Rock-salt lattices* (Fig. 144): LiX, NaX, KX (X = F, Cl, Br, I), RbCl, RbBr, RbI, CsF, NH_4Cl, NH_4Br, NH_4I, AgCl, AgBr; many binary oxides (MgO, CaO, SrO, BaO, CdO, MnO, NiO), sulphides (MgS, CaS, SrS, BaS, α-MnS, PbS), selenides (CaSe, SrSe, BaSe, MnSe, PbSe), tellurides (SrTe, BaTe, PbTe, SnTe), nitrides (TiN, ZrN, VN, NbN, TaN), carbides (TiC, ZrC, NbC), hydrides (HCl, LiH, NaH), and some intermetallic compounds (SnSb).

Some typical lattice structures.—The lattice structures of a large number of substances are now known and new determinations by the X-ray method are made daily. Only a few interesting and important examples can be described here (see R. C. Evans, *Crystal Chemistry*, 1939).

(1) The **diamond lattice** may be constructed by taking a face-centred cubic lattice of carbon atoms and inserting a carbon atom in the centre of each *alternate* cubelet, as shown in Fig. 148 (*a*). Each carbon atom forms the centre of a regular tetrahedron, the corners of which are occupied by four carbon atoms, as may be seen by drawing the lattice as in Fig. 148 (*b*). Diamond is an example of an **atomic lattice**, in which the atoms are linked by directed valency forces, as contrasted with the **ionic lattice** of an alkali halide, in which the separate charged ions are not linked by directed valencies but exert electrostatic forces on one another. Silicon and grey tin also crystallise in diamond lattices.

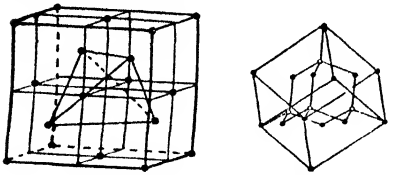


FIG. 148.—The diamond lattice.

(2) The **zinc blende lattice** is similar to that of diamond: each zinc atom is at the centre of a tetrahedron of sulphur atoms and each sulphur atom at the centre of a tetrahedron of zinc atoms. Many compounds crystallise in the zinc blende type of lattice: AgI, AlP, AlAs, AlN, AlSb, BeS, BeSe, BeTe, CSi, CdS, CdSe, CdTe, CuCl, CuBr, CuI, GaAs, GaSb, HgS, HgSe, HgTe, InSb, GaP, SnSb, ZnS, ZnSe, ZnTe.

(3) The **wurtzite lattice** (the second form of zinc sulphide) is formed from the zinc blende lattice by rotating alternate planes about an angle of 60° around the vertical axis. The tetrahedral symmetry is not disturbed, but the arrangement (Fig. 149) is different from that in diamond. The following compounds crystallise in the wurzite type of lattice: AgI, AlN, BeO, CdS, CdSe, CuH, NH_4F, ZnO, ZnS.

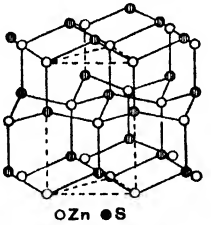


FIG. 149.—Wurtzite lattice.

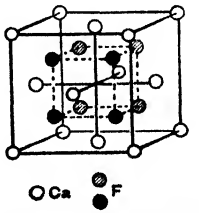


FIG. 150.—Fluorspar lattice.

(4) The **fluorspar lattice** has a face-centred lattice of calcium ions penetrated by a simple cubic lattice of fluorine ions, so that the corners of this lie on the quarter lengths of the diagonals joining the calcium ions (Fig. 150). Each Ca^{++} ion is surrounded by 8 F^- ions, each F^- ion by 4 Ca^{++} ions. In the elementary cube are $8/8 + 6/2 = 4$ Ca^{++} ions and 8 F^- ions (corresponding with the formula CaF_2). The F^- ions lie on the corners of a half-sized inner cube,

as shown. The following compounds crystallise in the fluorspar type of lattice: CaF_2, SrF_2, BaF_2, $SrCl_2$, CdF_2, PbF_2; CeO_2, PrO_2, ZrO_2, ThO_2, UO_2; Li_2O, Na_2O; Li_2S, Na_2S, Cu_2S, Cu_2Se; Mg_2Si, Mg_2Sn, Mg_2Pb.

An interesting cubic lattice is that of K_2PtCl_6 (Fig. 151). This may be regarded as a fluorspar lattice in which F^- is replaced by K^+, and each Ca^{++} by $PtCl_6^{--}$, in which the central Pt is surrounded by six Cl^- ions in octahedral arrangement, as previously assumed by Werner (p. 221). (For simplicity only one $PtCl_6^{--}$ is shown in full.) The compounds $[Co(NH_3)_6]I_2$, $K_2[PbCl_6]$ and $(NH_4)_2[SiF_6]$ crystallise in this type of lattice.

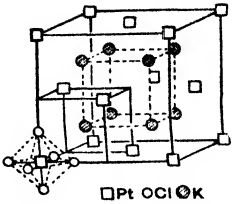


FIG. 151.—Lattice of K_2PtCl_6.

(5) The **graphite lattice** consists of flat hexagonal rings of carbon atoms arranged in equidistant layers, such that the atoms in alternate layers are in similar positions in the hexagons (Fig. 200, p. 443). Boron nitride BN crystallises in the graphite type of lattice.

(6) The **calcite lattice** (Fig. 152) may be regarded (not quite strictly) as a deformed rock-salt lattice. The latter is stood on a diagonal (looked at from above in the figure), all the Na^+ ions replaced by Ca^{++} ions and all the Cl^- ions by CO_3^{--} ions (consisting of carbon atoms each surrounded by a triangle of oxygen atoms in a plane at right angles to the diagonal, *i.e.* the plane of the paper), as shown. Then, on account of the space occupied by these ions, the cube expands in a horizontal direction and forms the cleavage rhombohedron (p. 232) of calcite. Calcium and carbon atoms are spaced at equal intervals along the crystal axis, and each carbon is surrounded by three oxygen atoms.

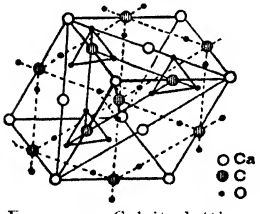


FIG. 152.—Calcite lattice.

(7) In the **nickel arsenide lattice** (Fig. 153), including the compounds FeS, FeSe, CoS, CoSe, CoTe, NiS, NiSe, NiTe, NiAs, NiSb, MnSb, TeSb, CoSb,

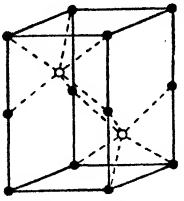


FIG. 153.—Nickel arsenide lattice.

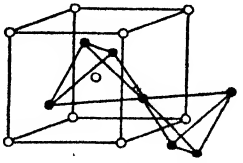


FIG. 154.—Cuprite lattice.

each metal atom is surrounded by six sulphur, selenium, arsenic, etc., atoms at the corners of a slightly distended octahedron, these atoms forming nearly regular tetrahedra not containing any metal atoms.

(8) In the **cuprite lattice** (known only for Cu_2O and Ag_2O) (Fig. 154) the oxygen atoms (○) form a body-centred cubic lattice and the metal atoms (●)

a face-centred cubic lattice. If an oxygen in the centre of each elementary cell is joined to the eight corners of the cube, then every second join is bisected by a metal atom so that each oxygen is surrounded by a regular tetrahedron of metal atoms. The elementary cube contains two oxygen and four metal atoms.

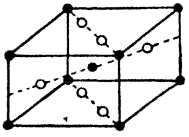


FIG. 155.—Rutile lattice.

(9) In the **rutile lattice** (Fig. 155) (ZnF_2, MnF_2, FeF_2, CoF_2, NiF_2, TiO_2, GeO_2, SnO_2, PbO_2, VO_2, NbO_2, TeO_2, MoO_2, WO_2, MnO_2, RuO_2, OsO_2, IrO_2) the metal atoms (•) form two body-centred simple tetragonal lattices. In each of these are two simple oxygen (○) lattices displaced by a parameter x along a face diagonal in opposite directions; the oxygen atoms belonging to one metal lattice lie on one diagonal and those belonging to the other metal lattice on the other diagonal.

The forms of all these lattices can really be appreciated only by an inspection of models, constructed of coloured wooden or other spheres (best of different sizes corresponding with the different atomic radii) joined by thick wires inserted into holes drilled in the spheres.

Mutual deformation of ions.—Measurements of refractive indices of solutions show that the electron shells of negative ions and of water molecules are less deformable when they are close to positive ions. The action of negative ions on positive ions is small, since positive ions are usually smaller and less deformable than negative ions. The *deformability* of a negative ion increases with increasing radius and increasing charge, whilst the *deforming action* of positive ions increases with decreasing radius and increasing charge.

If we consider the salts in the following table composed of cations in the vertical column and the anions in the horizontal row, also cations combined with water and ammonia, we may suppose the increasing depth of colour in the series fluoride to iodide is due to the increasing deformability of the anion, which is increasing in size. Sulphates have the same colour as the fluorides (with a small anion) because the O^{--} ions in SO_4^{--} are relatively fixed owing to the binding forces rendering them less deformable, whilst the oxides themselves, with more deformable O^{--} ions, are much darker in colour. According to Fajans, the blue colour of hydrated cupric salts is (at least in part) due to the deformation of water molecules.

	F	Cl	Br	I	O	S	SO_4	H_2O	NH_3
Ni++ -	Yellowish	Yellow-brown	Dark brown	Black	Dark green	Black	Grey-blue	Green	Blue
Cu++ -	White	Yellow-brown	Brown-black	—	Black	Blue-black	White	Blue	Blue
Ag+ -	Yellow	White	Yellow-white	Yellow	Dark brown	Black	White	Colourless	Colourless

Fajans (*Z. Elektrochem.*, 1928, **34**, 502) pointed out that *the tendency to form ionic or covalent links is related to the deformability of the electron shells.* Let a positive and negative *ion* be brought close together. If the deformation

of the electron shells reaches an actual transfer of electrons, a *covalent* link will be formed. This transfer depends on the attraction of the positive ion on the electrons of the negative ion, and on the firmness with which the latter are held. The attraction of the positive ion increases with its charge and is larger when the ion is small, so that the negative ion may approach nearer the charge of the positive ion core. The ease of separation of electrons from the negative ion increases with its size, outer electrons further from the positive core being less firmly held. Hence *the conditions for the formation of ionic and covalent links* may be summarised as follows:

IONIC	COVALENT
Positive charge low.	Positive charge high.
Large cation.	Small cation.
Small anion.	Large anion.

There are some apparent exceptions to Fajans's rule: fused mercuric chloride is non-conducting, although it should be ionic. This may be due to association.

The variation in interatomic distance among alkali halides is due to changes in ion radii, and no deformation of ions need be assumed; but when the cation is a small 18-electron shell ion (Cu^+, Ag^+, etc.) there is a much greater change in distance, which may be attributed to anion polarisation or covalent linking.

The number of negative as compared with positive *atomic* ions is small; in solutions and crystals only the following occur:

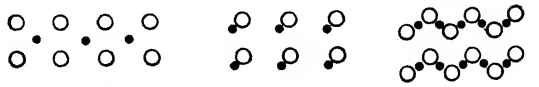
H^- (*e.g.* in LiH), F^-, Cl^-, Br^-, I^-, O^{--}, S^{--}, Se^{--}, Te^{--}, Po^{--},

and they are known only with external 8-electron shells; those with several valencies do not occur. The small number is supposed to be related to the tendency of anions with increasing charge to leave the ionic state on account of their greater deformability, although the energy changes in the formation of anions and cations are also of importance in this connection.

V. Goldschmidt (1926) pointed out that the distances between the atomic centres in polyatomic ions in crystals depend to some extent on the nature of the other ions in the lattice.

The distance N—O in the NO_3' ion is 1·40 A. in $NaNO_3$, but only 1·15 A. in $LiNO_3$, probably because the small lithium ion Li^+ has a stronger polarising effect than the larger sodium ion on the nitrate ion. The TiO_3 group in $CaTiO_3$ expands when the calcium is replaced by the smaller magnesium ion, and the $MgTiO_3$ structure is very like alumina, $AlAlO_3$, the magnesium and titanium being approximately equidistant from the nearest oxygens. In some cases the atoms round a polarising ion may be rearranged, as when the small beryllium ion replaces the calcium ion in spinel, $CaAl_2O_4$, when Ca'' and Al_2O_4'' are replaced by $[BeO_4]^{6-}$ and $2Al^{3+}$. X-ray measurements suggest that ammonium fluoride crystals do not consist of NH_4^+ and F' ions on the same plan as other ammonium halides, as the strong deforming action of the small fluorine ion on the ammonium ion causes a rearrangement to a "molecular compound," NH_3,HF.

Crystal structure and valency.—Solid crystals have been classified into the following groups (see Fig. 156):



(1) (2) (3)

FIG. 156.—Ionic or atomic, molecular, and layer lattices.

(1) **Ionic lattices** (salts) composed of *separate ions*, *e.g.* $Na^{\cdot}$, Cl'.

(2) **Molecular lattices** composed of *covalent molecules*, *e.g.* solid O_2, N_2, CO, NO, $CH_3{\cdot}CH_3$, in which the *intermolecular forces* (between the molecules) are different from the *intramolecular forces* (between the atoms in the molecules). Such crystals are usually non-conductors of electricity and relatively volatile, since the forces between the molecules are small.

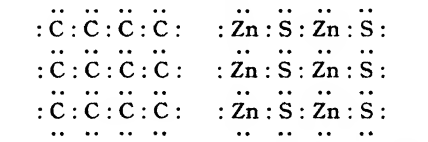
(3) **Layer lattices** made up of *large ions each associated with two small ions forming practically neutral layers* held together by weak non-polar forces and easily split into thin sheets (CdI_2, $Mg(OH)_2$, etc.).

(4) **Metals** and their compounds with one another, [Na], [Cu], [Cu_2Mg], perhaps [Pd_2H], in which the *positive ions form a lattice penetrated by negative electrons* (p. 249). These are conductors of electricity (since the electrons are mobile) and relatively non-volatile.

(5) According to Grimm and Sommerfeld, solid elements four places before an inert gas in the periodic system, also certain compounds of neighbouring elements, form atomic lattices with tetrahedral linkages, as in the **diamond lattice** (p. 242):

[C] [Si] [CSi] [Sn];
[AlN] [ZnS] [AgI];
perhaps [SiO_2] [Al_2O_3] [Si_3N_4] [P_3N_5].

These are mostly non-volatile, hard, and non-conducting, and the electrons are redistributed to give a tetrahedral arrangement of atoms:



Some of these compounds are now regarded as **interstitial compounds** (p. 253).

(6) Crystals of solid argon and other inert gas atoms in which the intermolecular forces are identical with the intramolecular forces, as in salts and metals, but are *non-ionic*. Forces of this type are sometimes called **van der Waals's forces** (p. 35).

Solid solutions.—Mixed crystals of potassium chloride and bromide give a *single* X-ray diagram very like that of both components and not a superposition of the diagrams of the two (Vegard, 1917). In the *ideal* case the atoms (or molecules) of a mixed crystal would be uniformly distributed. In the case of

alloys this state is attained only after long standing, annealing, etc., when the atoms change their positions in the crystal (p. 253). Vegard found that the replacement of one atom by another in mixed crystals is also irregular and unordered. In mixed crystals of potassium chloride and bromide the side of the elementary cubic lattice a_m is accurately given by a linear relation (**Vegard's law**, 1921):

$$a_m = a_{KBr}(p - 100)/100 + a_{KCl}\,p/100$$

where p = mol p.c. of KCl in the mixed crystal, and a_{KCl}, a_{KBr} are the lengths of the sides of the KCl and KBr lattices.

According to Grimm (1921) mixed crystals are formed when: (i) the chemical type is the same (*e.g.* NaCl, PbS; $BaSO_4$, $KMnO_4$), (ii) the lattice type is the same, and (iii) the atomic or ionic distances are similar, the necessary degree of similarity depending on the temperature and the type of linking.

Isomorphism.—Cases of isomorphism difficult to understand on the basis of the old structural formulae, *e.g.* $CaCO_3$ and $NaNO_3$:

become clearer when electronic formulae of the ions are considered, *e.g.* (see, however, p. 270):

The ions F^- and O^{--} both have completed octets of the neon structure, as have Na^+ and Mg^{++}, and NaF and MgO are isomorphous. These ions with identical outer electron configurations are called *isosteres* by Langmuir (*J.A.C.S.*, 1919, **41**, 1543), who gives examples of isomorphism based on isosterism:

MgO NaF	KCNO KN_3
MgF_2 Na_2O	$NaClO_3$ $CaSO_3$
$CaCl_2$ K_2S	$KHSO_3$ $SrHPO_3$
KCl CaS	$Na_2S_2O_7$ $Ca_2P_2O_7$
$RbMnO_4$ $BaCrO_4$	

and another case is isomorphism due to the BeF_4'', PO_3F'' and SO_4'' ions, with similar electronic arrangements.

Argon and methane have similar physical properties; the K^+ ion, which is isosteric with A but has one positive charge, should thus resemble the NH_4^+ ion which is isosteric with methane. The K^+ ion is not isosteric with the NH_4^+ ion which, like methane, has tetrahedral symmetry. In KCl crystals each K^+ ion is surrounded by *six* equidistant Cl^- ions, whilst in NH_4Cl crystals each NH_4^+ ion is surrounded by *eight* equidistant Cl^- ions arranged at the corners of a cube with NH_4^+ at the centre. Potassium and ammonium sulphates, however, are isomorphous, so that the larger sulphate ions constrain the K^+ and NH_4^+ ions into like positions.

Ionic size and crystal structure.—In a lattice formed of two types of atoms or ions A and B, the number of atoms of B arranged round any given atom of A is called by crystallographers the *coordination number* of A. It depends on the radii of A and B. In NaCl the small Na^+ ion ($r = 0{\cdot}98$ A.) allows six Cl' ions ($r = 1{\cdot}81$ A.) to pack around it, whilst the large Cs^+ ion ($r = 1{\cdot}65$ A.) can accommodate eight chlorine ions. The coordination numbers of Na and Cs in NaCl and CsCl are 6 and 8. In SiO_2 the small Si^{4+} ion ($r = 0{\cdot}39$ A.) fits into the space in the centre between four large O^{2-} ions ($r = 1{\cdot}32$ A.) arranged tetrahedrally and its coordination number is 4. Each oxygen is shared by two silicons, so that the coordination number of oxygen in silica is two.

V. Goldschmidt (*Ber.*, 1927, **60**, 1263; *T. Faraday Soc.*, 1929, **25**, 253; *J.C.S.*, 1937, 655; Pauling, *The Nature of the Chemical Bond*, 1940, 367 f.) showed that *the coordination number is regulated by the relative sizes of the ions.* The extreme ratios of the two ionic radii for different coordination numbers are:

Coord. no. -	3	4	6	8	12
r_1/r_2 -	0·15	0·225	0·414	0·732	1·000

The numbers 5, 7, 9, 10 and 11 are excluded by geometry if the charges are to balance.

For a particular ion the coordination number may vary with the other ion, owing to polarisability, and in some cases a molecular lattice may be formed (p. 244).

Radii of ions as given by Goldschmidt are (in A.):

0·1–0·3 B^{3+} C^{4+} N^{5+} S^{6+}.
0·3–0·5 Be^{2+} Si^{4+} Ge^{4+} P^{5+} V^{5+} Mo^{6+} W^{6+}.
0·5–0·7 Al^{3+} Ga^{3+} Fe^{3+} Cr^{3+} V^{3+} Ti^{4+} Nb^{5+} Ta^{5+}.
0·7–0·9 Li^+ Mg^{2+} Ni^{2+} Co^{2+} Fe^{2+} Zn^{2+} Sc^{3+} In^{3+} Zr^{4+} Hf^{4+} Sn^{4+} } Mn^{2+}.
0·9–1·1 Na^+ Ca^{2+} Cd^{2+} Y^{3+} Gd^{3+} – Lu^{3+} Ce^{4+} Th^{4+} U^{4+} }
1·1–1·4 K^+ Sr^{2+} La^{3+} – Eu^{3+}.
1·4–1·7 Rb^+ Tl^+ Cs^+ Ba^{2+} Ra^{2+}.

Elements of similar ionic radii, and preferably though not necessarily of the same ionic charge, replace one another in minerals. In some cases (Zr and Hf; Y and Ho) where the radii, charges and ionic types are nearly alike, the elements always occur together. If the radii are similar but the charges different, adjustment of the lattice may occur, and an ion of greater charge is more readily included than one of smaller charge; *e.g.* in the crystallisation of magnesium minerals, scandium occurs in the first crystals and lithium in the last.

According to Goldschmidt the **hardness** of crystalline substances of the same formula type decreases with increasing distances of the particles and increases with the valencies, whether the substances form atomic or ionic lattices and with covalent or ionic bonds. This indicates that the hardness arises from electrostatic attractions.

METALS

Gold, silver, copper, iron, tin, antimony and lead were known to the ancient Egyptians and Babylonians and are mentioned in the Old Testament and by early Greek authors (Partington, *Origins and Development of Applied Chemistry*, 1935). Mercury is mentioned by Aristotle (384–322 B.C.), zinc by Strabo (7 B.C.) and bismuth by Agricola (1530 A.D). The remaining metals were discovered since the seventeenth century. Mercury was regarded as a true metal after its solidification by cold, noticed by Braune in a severe Russian winter in 1759.

Only a few metals occur native ; the rest are found as ores, mostly oxides and sulphides, or carbonates and sulphates. The principal methods used for the *extraction of metals* are :

(1) *Reduction of oxides with hydrogen* : all metals with atomic weights greater than that of manganese.

(2) *Reduction of oxides with carbon* : copper, zinc, cadmium, aluminium (electrolytic), tin, lead, bismuth, manganese, iron, cobalt, nickel ; titanium, zirconium, thorium in the electric furnace ; special steels by simultaneous reduction of oxides with carbon and iron ; metals after group III, some at high temperature in the electric furnace. In some cases carbon monoxide is the actual reducing agent.

(3) *Reduction of oxides with aluminium* (*thermit process*) : cerium, vanadium, chromium, molybdenum, manganese. On the small scale magnesium or mixed-metal (p. 434) may replace aluminium.

(4) *Oxidation of sulphides* (*a*) directly by atmospheric oxygen ($HgS + O_2 = Hg + SO_2$) or (*b*) by partial oxidation and interaction of sulphide with oxide or sulphate (copper and lead).

(5) *Reduction of sulphides with iron* : mercury, lead, antimony.

(6) *Electrolytic processes* : electrolysis of (*a*) fused hydroxide (sodium, potassium, etc.) ; (*b*) fused chloride (beryllium, magnesium and alkaline earth metals) or the oxide dissolved in fused cryolite for aluminium ; (*c*) solutions of salts (copper, silver, gold, zinc, nickel, chromium ; with a mercury cathode for several metals, followed by heating the amalgam).

(7) *Carbonyl process* for nickel.

The metallic state.—Maxwell recognised that the opacity of metals is connected with their good conducting power for electricity, and Lorentz accounted for their electrical and thermal conductivities by assuming that they contain free mobile electrons, behaving like gas atoms, together with massive positive ions. The electric current through a metal is carried entirely by the free electrons, which are emitted by heated metals (*thermionic emission*). The difficulty that the electrons appear to contribute nothing to the heat energy (p. 224) was explained by Sommerfeld (1928) on the basis of Fermi's quantum theory of gases (1926), according to which the heat energy of electrons in metals is very small because of their very small mass (see p. 251).

Alloys

The existence of definite compounds of metals (*intermetallic compounds*) has long been recognised (Hedges, *Ann. Rep. C.S.*, 1935, **32**, 165). Some relations between the capacity for forming compounds and the positions of the metals in the periodic system were given by Tammann :

(i) A metal rarely combines with another of the same group and never with another of the same sub-group.
(ii) A metal combines with all the members of a sub-group or with none of them (there are exceptions to this).

The *formulae of intermetallic compounds* have no relation to the ordinary valencies of the metals and are usually fairly simple. The substitution of an atom of one metal in a binary alloy by an atom of another metal of the same group will not change the number of valency electrons, and if the atomic radii are approximately the same very little distortion is produced in the crystal lattice ;* there will thus be a tendency to form an unbroken series of solid solutions, and little disposition to form compounds.

Metals in any given sub-group may be expected to show the same type of phase diagram in alloys with a given metal, and compounds with this metal usually have analogous formulae :

CuZn (or Cu_6Zn_5)	Cu_5Zn_8	$CuZn_3$
AgZn	Ag_5Zn_8	$AgZn_3$
AuZn	Au_5Zn_8	$AuZn_3$

When one atom is replaced by another of different valency, the phase diagram shows that a solid solution phase exists only in a limited composition range (which usually includes a simple atomic ratio), beyond which a new phase appears. Carpenter in 1915 showed for Cu-Zn, Ag-Zn, Ag-Cd systems, etc., that the phases follow one another in a regular order on the diagram as the amount of the second metal increases, and X-ray spectra show that the successive phases have characteristic structures. The phase order is :

(i) α-phase : face-centred cubic lattice.
(ii) β-phase : body-centred cubic lattice.
(iii) γ-phase : cubic lattice with a large number of atoms in the unit cell.
(iv) ϵ-phase : hexagonal close-packed lattice.

In some cases the lattice of (ii) is a more complex cubic lattice of the β-manganese structure (p. 241), and there are exceptions to this succession of β-, γ- and ϵ-phases when the atomic radii exert a determining influence, as in alloys of cadmium with alkali metals.

Some regularities which govern the composition of these β-, γ- and ϵ-alloy phases were discovered empirically by Hume-Rothery (1926), Bradley (1928), and Westgren and Phragmén (1929). If μ is the total number of valency electrons, ν the total number of atoms, then the ratio $\lambda = (\text{total no. of valency}$

electrons/total no. of atoms) $= \mu/\nu$ has characteristic values for the β-, γ- and ϵ-phases :

(i) β-phase : $\lambda = 3/2$. Thus for CuZn $\mu = 1 + 2 = 3$, $\nu = 2$; for Cu_5Si $\mu = 5 + 4 = 9$, $\nu = 6$; for Cu_3Al and Ag_3Al $\mu = 3 + 3 = 6$, $\nu = 4$. The 3/2 ratio is usually maintained in the β-phases of the systems Ag-Mg, Ag-Zn, Ag-Cd, Au-Zn, Au-Cd, Cu-Al, Cu-Zn, Cu-Sn.

(ii) γ-phases : $\lambda = 21/13$. Thus in the γ-phases of the Cu-Zn and Cu-Al systems, Cu_5Zn_8 and Cu_9Al_4, μ is $5 + 16 = 21$, and $9 + 12 = 21$, and ν is $5 + 8 = 13$, and $9 + 4 = 13$, respectively, hence $\lambda = \mu/\nu = 21/13$. In the Cu-Sn system the γ-phase is $Cu_{31}Sn_8$ with $\mu = 31 + 32 = 63$, and $\nu = 39$, and the γ-phases in the systems Ag-Zn, Au-Zn, Ag-Cd, Ag-Hg, and Cu-Cd have λ approximately 21/13. Even in ternary alloys (composed of three metals) the γ-phases Cu_5Zn_8Al and $Cu_5Zn_8Al_2$ have $\mu = 6 + 12 + 3 = 21$ and $\mu = 8 + 4 + 9 = 21$, and $\nu = 13$ in each case. (It should be noted that copper is assumed to have its lowest and tin its highest valency in the Cu-Sn compounds. Some β and γ structures have not the correct λ ratios ; many binary systems have the correct ratio but no γ-phase is known.)

(iii) ϵ-phase : $\lambda = 7/4$. Thus in $CuZn_3$, $AgZn_3$, $AgCd_3$, and in the systems Ag-Al, Au-Al, Ag-In, Cu-Sn, Ag-Sn, Cu-Sb and Ag-Sb, the ϵ-phases have $\lambda = \mu/\nu = 7/4$ in most cases.

In the β- and γ-phase compounds of the transition metals Fe, Co, Ni, Pd, Rh, the valency of the transitional element must be taken as zero if the rules are to apply, *i.e.* its atom contributes no valency electrons to the alloy structure :

(β) : CoAl, FeAl, NiAl, $\mu = 0 + 3 = 3$, $\nu = 2$, $\therefore \lambda = 3/2$;
$CoZn_3$, $\mu = 0 + 6$, $\nu = 4$, $\therefore \lambda = 3/2$.

(γ) : Co_5Zn_{21}, Ni_5Zn_{21}, Pt_5Zn_{21}, Rh_5Zn_{21} ;
$\mu = 0 + 42 = 42$, $\nu = 26$, $\therefore \lambda = 21/13$.

This behaviour is analogous to the formation of carbonyls (p. 875), in which *all* the valency electrons are supplied by the coordinated carbon monoxide molecules. (The following sections presuppose a knowledge of material in Chapter X.)

In the atoms of the metals of the first transitional series (p. 176) the $3d$ quantum level (see p. 258) is nearly complete. Nickel, apart from the completed lower levels, has three possible electronic configurations :

$$3d^84s^2, \qquad 3d^94s, \qquad 3d^{10},$$

in which the atom has 2, 1 or 0 effective valency (s) electrons. The ground state is $3d^94s$, but as the $3d^{10}$ state has only 1·25 electron-volts * more energy than this, and as the binding energy of the atom in the lattice is about 4 electron-volts, it is possible for the nickel atom to combine in the $3d^{10}$ state, and thus contribute no valency electrons to the alloy structure.

The quantum theory of metals.—It is obviously not possible to regard the atom bindings in alloys as ordinary covalent links formed by electron-sharing, since (i) the characteristic metallic properties which are regarded as due to *free*

* The energy acquired by an electron in moving under a fall of potential of 1 volt ; it is $1{\cdot}6 \times 10^{-12}$ erg.

electrons (p. 249) are retained, (ii) the number of atoms surrounding a central atom (12 in the face-centred cubic and close-packed hexagonal lattices) is much larger than the number of valency electrons available on the central atom, (iii) the formulae do not agree with the ordinary valencies.

The structures of alloys can be elucidated by the electron theory of metals, which is based on Pauli's principle (p. 257) (Mott and Jones, *The Theory of the Properties of Metals and Alloys*, 1936; A. H. Wilson, *The Theory of Metals*, 1936; Bernal, *Ann. Rep. C.S.*, 1935; Anderson, *J.S.C.I.*, 1937, **56**, 677R.). The electrons in the metal conform to Pauli's principle, and in a metal crystal containing N atoms the electrons are held in common by all the atoms. They occupy a large number of energy states or " cells ", each of which, according to Pauli's principle, can contain only two electrons with opposite spins. At absolute zero, each of the first $N/2$ cells is so filled. At higher temperatures some electrons are " promoted " to higher energy levels.

The electric field rises to a maximum at each positive ion and is a minimum between each pair of positive ions. The wave character of the electron (p. 265) then restricts the electron energies to certain " permitted " energy bands called *Brillouin zones*, between which are empty bands of " forbidden " energies, to cross which usually requires a large energy. The breadth of a band depends on the overlap of the electron wave functions. This is large for the outer valency electrons, which lie on a large number of energy levels closely spaced in the permitted band, each band replacing the single energy level in an isolated atom. The number of electrons which can occupy the Brillouin zone of lowest energy depends on the lattice structure. Before the lowest zone is filled with electron pairs of opposite spins, however, the energies of the electrons last added rise so sharply that they tend to pass into the second zone, and this effect is related to the whole-number λ-ratios (p. 251).

The lattice structure may also change so as to offer more electronic states per atom than the first Brillouin zone, and this corresponds with the remarkable sequence of phases ($\alpha \rightarrow \beta \rightarrow \gamma \rightarrow \epsilon$) of a binary alloy. The maximum number of electrons per atom in the first zone is calculated as in the region of 1·480, 1·538 and 1·75 for the β-, γ-, and ϵ-phases, corresponding with the λ-ratios $3/2 = 1{\cdot}5$, $21/13 = 1{\cdot}615$ and $7/4 = 1{\cdot}75$, respectively.

Berthollide compounds.—The law of fixed proportions applies to compounds formed by ordinary valency bonds, or to salts formed from positive and negative ions. In solids the size of the atoms and the size and shape of the ions or molecules affect the geometrical packing.

(i) When the sizes are very different and the components are well packed together solids of definite composition such as alums are formed, but these decompose in solution. Compounds of constant composition are sometimes called *Daltonian compounds*.

(ii) When the crystal units are nearly alike in size and shape they may occupy positions indifferently without affecting the crystal structure, and size then replaces electric charge and valency in determining the composition and structure (see Bernal, *Ann. Rep. C.S.*, 1933, 381). In lithium ferrite $LiFeO_2$ with the rock-salt structure (Fig. 144), Li^+ (radius 0·78 A.) and Fe^{3+} (radius 0·67 A.) ions occupy the cation positions indifferently, and in the spinels $[M_1]_2^{4+}[M_2]^{2+}O_4$ the cations

M_1^{3+} and M_2^{2+} must satisfy the crystal coordination rules (p. 248) and balance the charge on the oxygen, or when the cation charge is deficient O^{--} is replaced by OH^- or F^-. Thus ($Nb^{5+}Fe^{2+}$) can be replaced by ($Ti^{4+}Fe^{3+}$). This holds for the spinels $MgFe_2O_4$, $MgGa_2O_4$, $MgIn_2O_4$, $TiMg_2O_4$, $TiFe_2O_4$, $SnZn_2O_4$, but not for the typical spinel $MgAl_2O_4$, nor for the aluminates of Mn, Fe, Co, Ni and Zn. Even crystals of C_6H_4ClBr are indistinguishable by X-ray methods from an equimolecular homogeneous crystal of *p*-dichlorobenzene $C_6H_4Cl_2$ and *p*-dibromobenzene $C_6H_4Br_2$.

The interchangeability of atoms is very marked in alloys. Metals crystallising in face-centred lattices form solid solutions, usually in all proportions, although silver has an exceptionally low miscibility in view of the close agreement of its atomic radius with that of gold. In the resulting lattice the atoms occupy the corners and face-centres of a cube, but do so indifferently, any atom being able to occupy any place at temperatures not too far below the melting point; on cooling slowly a rearrangement of the atoms may occur.

In the mixture Cu_3Au between 960° (m.p.) and 390° the atoms occupy the points indifferently, but below 390° the gold atoms move to the cube corners and the copper atoms to the cube faces.

Such ordered arrangements, called *superstructures* (or *super-lattices*) differ from solid solutions in mechanical, magnetic and electrical properties. The melting point is a maximum, and might be mistaken on the phase diagram for that of a definite compound. For such substances the name *Berthollide compounds* (see p. 4) was introduced by Kurnakow (*Z. anorg. Chem.*, 1914, **88**, 109), and the group has been much increased by later investigations.

Among Berthollide compounds are the *interstitial compounds* in which transitional metals admit small atoms (H, B, C, N) into the interstices of the lattice, either statistically distributed or in definite positions; these may be called "addition" crystal compounds (or solid solutions) and formulated *e.g.* as $[Pd]H_{\frac{1}{2}}$ or $[Fe]N_x$. Another type is the "subtraction" compound (or solid solution) exemplified in the systems Fe-S, Fe-Se, and Fe-O, in which there is a range of solid solutions on the iron-poor side of FeS, FeSe and FeO, and compounds of these *exact* compositions do not seem to exist. The lattice shrinks as the iron content is reduced and it behaves as an ideal FeS, FeSe or FeO lattice from which an increasing number of iron atoms have been removed to form spaces, which are partly filled by adjustments of the other atoms. To preserve electroneutrality, it may be assumed, some ferrous atoms become ferric, *e.g.* $(Fe^{II}, Fe^{III})_{1-x}O$; if three ferrous atoms are replaced by two ferric, the charge will balance that on three oxygen atoms. The γ-structures of Cu_5Zn_8, Cu_9Al_4, etc. (p. 251), may be regarded as subtraction solid solutions.

Metallic polyanions.—A solution of sodium in liquid ammonia (p. 317) dissolves lead to form a conducting solution, and a similar solution is formed by adding excess of sodium to a solution of lead iodide in liquid ammonia. The metals of Groups I (except alkali metals) to III form alloys insoluble in liquid ammonia, but other metals besides lead which form gaseous hydrides (p. 179) behave like lead in the above respect.

The soluble compounds may be regarded as containing complex *metallic polyanions* corresponding with polyhalides (p. 305) or polysulphides (p. 313), and these may have intense colours in liquid ammonia. Polyanionic salts are extracted by liquid ammonia from fine-grained alloys of sodium with the metals, and on evaporation form pyrophoric solids of metallic appearance, containing ammonia. Some typical compounds may be formulated :

$$Na_3[As(As)_6] \quad Na_3[Bi(Bi)_4] \quad Na_4[Sn(Sn)_8] \quad Na_4[Pb(Pb)_8].$$

When the ammonia they contain is removed they decompose into simpler alloys, *e.g.* $[Na(NH_3)_x]_3Sb_3$ gives NaSb (Zintl, 1932–3).

CHAPTER X

THE QUANTUM THEORY OF THE ATOM

SINCE its enunciation by Frankland in 1852 the idea of valency has been a guiding star in chemical research. The elementary conception of the saturation capacity of atoms, and the use of structural formulae in which bonds replace numerical valencies, have served chemists well over a long period of years, and the addition of the ideas of directed bonds by van't Hoff and of the cyclic structure of benzene by Kekulé enabled the organic chemist to produce models for numerous molecules, most of which are now known by refined physical research to be essentially correct. This research added *quantitative* data in the shape of atomic and molecular dimensions, bond angles, and a clearer idea of the different types of linkage, but until recently it added very little to conceptions already familiar to the chemist.

Chemists have naturally speculated freely on the nature of valency, and since the discovery of the electron in 1897 many "electronic theories of valency" were proposed, culminating in the electron-pair theory of G. N. Lewis (1916), which still possesses vitality and promise. Three years after the discovery of the electron came the quantum theory of Planck (1900), which has since completely revolutionised Physics. It is in the conceptions of the quantum theory that the most recent developments of the theory of valency must be sought. These are more subtle and difficult than most conceptions employed by chemists, and in the following sketch only an outline of the subject can be given. As is so often the case, an historical order of development seems to offer advantages, and hence the theory of Bohr, although it is now abandoned in its detailed features, calls first for consideration.

QUANTUM NUMBERS

According to Bohr's theory (1913) the hydrogen atom (atomic number = 1) consists of one electron of mass m and charge $-e$ revolving around a nuclear proton of charge $+e$. If the nucleus behaved like a central sun and the electron like a planet subject to gravitational force, *any* orbit would be possible, each with an appropriate kinetic energy of the planet which would keep it in that orbit against the pull of gravitation tending to drag it into the sun. In the case of the *charged* proton and electron this is not possible, since the moving electron would give out radiation, gradually lose energy and fall spirally into the nucleus. Bohr had thus to assume that there is a limited number of *stationary orbits*, in each of which the electron rotates without radiation, whilst when it passes from one orbit to another in which it has less energy it emits radiation of definite frequency. If we imagine the electron starting at an infinite distance it will pass into successive orbits each nearer the nucleus, giving off energy between each transition until it arrives at the smallest possible orbit, nearest the nucleus, when the atom is said to be in the ***normal state.***

By convention, in Bohr's theory, the energy of the electron at an infinite distance from the nucleus is put equal to zero, so that its energy E in an orbit will be negative. In other cases the energy in the normal (or " ground ") state is taken as zero, and in what follows the two different conventions should be kept in mind.

The possible orbits are circles with the nucleus at the centre. Each is characterised by a **quantum number** n, which determines the energy of the electron according to, and is itself defined by, the equation :

$$E_n = -K\mathbf{h}/n^2, \quad \ldots\ldots(1)$$

where K is a constant, having for the hydrogen atom the value :

$$K = 2\pi^2 e^4 m/\mathbf{h}^3 = 3{\cdot}29 \times 10^{15}, \quad \ldots\ldots(2)$$

h being Planck's constant (p. 226). In passing from an orbit of quantum number n_2 to one of quantum number n_1 ($n_2 > n_1$), the energy given out is therefore :

$$E_2 - E_1 = \Delta E = K\mathbf{h}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right), \quad \ldots\ldots(3)$$

and by the quantum equation the *frequency of the radiation* emitted will be :

$$\nu = \Delta E/\mathbf{h} = K\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right). \quad \ldots\ldots(4)$$

The values of n for circular orbits increase with increasing distance of an electron from the nucleus, and hence small values of n correspond with firmer binding of the electron to the nucleus, the electrons closest to the nucleus having $n = 1$, etc.

When n_1 is given a small whole number value, such as 1, 2 or 3, and n_2 is given a series of higher whole number values (*e.g.* $n_1 = 2$; $n_2 = 3, 4, 5, \ldots \infty$), equation (4) gives with great accuracy the frequencies (or wave-lengths) of the lines in each of the various spectral series of hydrogen (*e.g.* with the values just quoted, the various lines of the Balmer series). Thus n is always a whole number from 1 to infinity ; $-K/n^2$ is called a **term.**

If the nucleus has a charge $+Ze$ (Z = atomic number), and there is still a single electron rotating about it, the value of K in (4) is replaced by Z^2K, *e.g.* for the singly ionised helium atom ($Z = 2$) the spectra are given by (4) with $4K$ instead of K. This is true only for a single outer electron, otherwise the electrons exert a screening effect on the positive charge of the nucleus.

Still confining our attention to the hydrogen atom we recall that the actual orbit of a planet is an ellipse with the sun at a focus, and as well as circular electronic orbits we may also have *elliptical orbits*, in which the electron has the same energy as in a corresponding circular orbit. Each orbit will, by (1), be characterised by a **principal quantum number** n, but each ellipse for a given value of n requires another number k for its definition, called a **subsidiary quantum number** : k has also whole number values (zero excluded) up to n. The ratio n/k is equal to the ratio of the major to the minor axis of the ellipse. The orbit for which $n = k$ is always a circle.

If an orbit is denoted by n_k, the orbit n_n is a circle. For a given value of n, the quantum number k may have n values, 1, 2, 3, ... n. For $n=4$ we may have $k=1$, 2, 3, 4, and four possible orbits, one circle 4_4 and three ellipses 4_1, 4_2 and 4_3, in which the ratios of the major to the minor axes are 4 : 1, 4 : 2 and 4 : 3, respectively. These orbits are shown in Fig. 157, together with the 1_1; 2_1, 2_2; and 3_1, 3_2, 3_3 orbits.

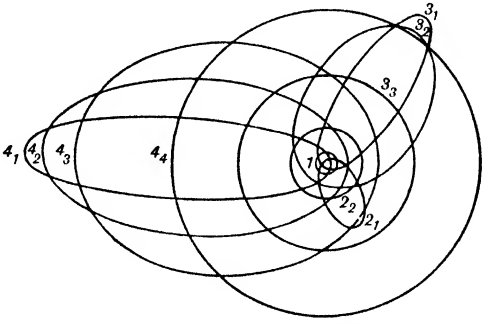


FIG. 157.—Bohr orbits of hydrogen atom.

In place of Bohr's k the new quantum theory introduces a **serial** (or **azimuthal**) **quantum number** l, which is always 1 less than k and has the values 0, 1, 2, ... $(n-1)$.

The splitting of spectrum lines in a magnetic field (*Zeeman effect*) introduces a third or **magnetic quantum number** m_l, which defines the angle between the plane of the electron orbit (defined by n and l) and the direction of the magnetic field. The values of m_l are

$$l,\ (l-1),\ (l-2),\ \ldots\ 1,\ 0,\ -1,\ \ldots\ (-l+1),\ -l,$$

or $(2l+1)$ values for each value of l.

That the angle between the electron orbit and the direction of a magnetic field has only discontinuous values, corresponding with the step-wise change of m_l, was proved by Stern and Gerlach (1922), who found that a beam of silver atoms when passed through a very inhomogeneous magnetic field in a vacuum furnace split into two beams, on opposite sides of the undeflected beam and corresponding with two angular positions of the plane of the electron orbit with respect to the field direction.

A fourth or **spin quantum number** s is required to explain the *fine structure* of spectrum lines, each hydrogen line *e.g.* consisting of two very close together and only separated by apparatus of high resolving power. The quantum number s defines the *spin* of the electron about its own axis, which may be in one of two directions and s has only two values : $+\frac{1}{2}$ and $-\frac{1}{2}$.

For an atom containing more than one electron, the maximum number of electrons in each shell is fixed by **Pauli's exclusion principle** (1925), which states that ***in any one atom there is never more than one electron with a given set of quantum numbers, n, l, m_l, and s.*** If two electrons, *e.g.*, have n, l, and m_l the same, then for one $s=+\frac{1}{2}$ and for the other $s=-\frac{1}{2}$.

If $n=1$, then $l=0$ and $m_l=0$. There are two values of s, viz. $+\frac{1}{2}$ and $-\frac{1}{2}$, hence there can be only *two* electrons of principal quantum number $n=1$.

If $n=2$, then $l=0$ or 1. For $l=0$, $m_l=0$ and $s=\pm\frac{1}{2}$ For $l=1$, m_l has the possible values 1, 0, -1. Each of these can be associated with two values of s, $\pm\frac{1}{2}$, giving six possible cases, and with the two for $l=0$ eight in all.

If $n=3$, l can be 0, 1 and 2, and the values of m_l for the three cases are 0, (1, 0, -1), and (2, 1, 0, -1, -2), respectively, or 9 in all. Each can have the two values $\pm\frac{1}{2}$ of s, making a total of 18.

If $n=4$, l can be 0, 1, 2 and 3, and the values of m_l for the four cases are 0,(1, 0, -1), (2, 1, 0, -1, -2) and (3, 2, 1, 0, -1, -2, -3), respectively, or 16 in all. Each of these can have the two values, $\pm\frac{1}{2}$, of s, making a total of 32.

Since the maximum number of values of m_l is $(2l+1)$ and each can be associated with the two values of s, $\pm\frac{1}{2}$, the maximum number of electrons * in a sub-group is $2(2l+1)$:

TABLE I

Level n_l	1_0	2_0	2_1	3_0	3_1	3_2	4_0	4_1	4_2	4_3
l	0	0	1	0	1	2	0	1	2	3
Max. no. of electrons	2	2	6	2	6	10	2	6	10	14
	2	8		18			32			

The maximum number of electrons with the given quantum numbers allowed for any atom, derived, as explained, from Pauli's exclusion principle, is given in the last line.

In spectrum notation (summary in *Ann. Rep. C.S.*, 1933, 56) letters are used to denote the values of the quantum number l:

l	0	1	2	3	4	5
Symbol	s	p	d	f	g	h

Thus a $3p$ electron has $n=3$ and $l=1$. (The symbol s is also used for the spin quantum number, and the two uses must not be confused.) An upper index denotes the number of electrons in the given state: thus $1s^2 2p^4$ (read " two in 1s," etc.) means two electrons with $n=1$ and $l=0$, and four electrons with $n=2$ and $l=1$.

An *inner quantum number* j is defined as:

$$j=l+s$$

where s has the values $+\frac{1}{2}$ or $-\frac{1}{2}$, except for $l=0$, when it has the value of $+\frac{1}{2}$ only. Thus for each value of l (except $l=0$) there are *two* values of j and these are half-integral:

l	0	1	2	3	4
j	$\frac{1}{2}$	$\frac{3}{2}$ $\frac{1}{2}$	$\frac{5}{2}$ $\frac{3}{2}$	$\frac{7}{2}$ $\frac{5}{2}$	$\frac{9}{2}$ $\frac{7}{2}$

* From the point of view of wave mechanics (p. 265) this number gives the number of possible *orbits* which can accommodate electrons, but the distinction is hardly significant at this stage.

The Periodic Table

Since the numbers of electrons in the groups in Table I correspond with the numbers of elements in the periods of the periodic table :

2 8 8 18 18 32 [6]

it was at first thought that, as each period (except the last incomplete period) ends with an inert gas :

He Ne A Kr Xe Rn —

the numbers should give the numbers of electrons in the outer electron shells of the inert gases. It is now known that *the outer electron group is* 8 *for all the inert gases*, and hence after argon some of the inner shells of electrons must be left incomplete whilst an 8-electron shell builds up over them (p. 209).

The successive electron shells, starting with the one nearest the nucleus, are symbolised in X-ray notation (p. 191) as *K*, *L*, *M*, *N*, *O*, *P* and *Q*.

The group of 2 electrons with $n=1$ completed with helium forms a *K*-shell nearest the nucleus which is present in the atoms of all the other elements. Above this, a shell of from 1 to 8 electrons is completed from lithium to neon, the nuclear charge increasing in steps of 1, and the mass by larger steps by addition of both protons and nutrons to the nucleus (p. 208). These 8 electrons with $n=2$ complete a second or *L*-shell. A third or *M*-shell of 8 electrons with $n=3$ is formed on passing from sodium to argon.

The electrons in each group with the same principal quantum number n are not all equivalent, as they have different values of the serial quantum number l, as required by Pauli's principle. In Li there is one $2s$ electron ($n=2$, $l=0$), in Be two, and this is the maximum number. They are valency electrons. Of the three $n=2$ electrons in B there are two $2s$ and the third must be a $2p$ ($n=2$, $l=1$) electron. There can be six $2p$ electrons, and this maximum is reached with neon. Fluorine and oxygen atoms tend to bind these electrons to reach a stable neon structure, but as their nuclear charges are only 7 and 6, respectively, they then form the negative ions F^- and O^{--}, neon with a nuclear charge of 8 being neutral with 8 outer electrons.

In the next period $n=3$ and the electrons form an *M*-shell. Na has one $3s$ electron, Mg two, and this is the maximum number for $n=3$, $l=0$. In Al the third electron is a $3p$ ($n=3$, $l=1$), and the six $3p$ electrons possible have been added when A is reached.

The next period is a long period of 18 elements. In K the first electron goes into a $4s$ level, the ten $3d$ ($n=3$, $l=2$) levels being left empty for the time, since the energy in a $4s$ level is lower than that in a $3d$.

In Fig. 158 the term values (p. 256) in cm.$^{-1}$ of the lines (some doublets) for the alkali metals are shown.* The numbers against the small circles give the

*The values of n^* on the right are the "effective quantum numbers," such that the terms are $-K/n^{*2}$. They differ from whole numbers owing to the screening effect of electrons nearer the nucleus on the effective charge of the latter.

values of n, *e.g.* the circles in the first vertical line, counting from below, denote $2s$, $3s$, $4s$ and $5s$ electrons, in the second line $2p$, $3p$, $4p$ and $5p$ electrons, etc. The energy increases from below upwards, so that a $2s$ electron in Li has less energy than a $2p$. It is seen that for K the $4s$ and $4p$ terms are much lower than the $3d$, so that in passing from A to K the electron goes into a $4s$ level, leaving the $3d$ level empty. With Rb the $5s$ level is preferred to the $4d$ and $4f$ ($n=4$, $l=3$) levels, and with Cs the $6s$ to the $5d$.

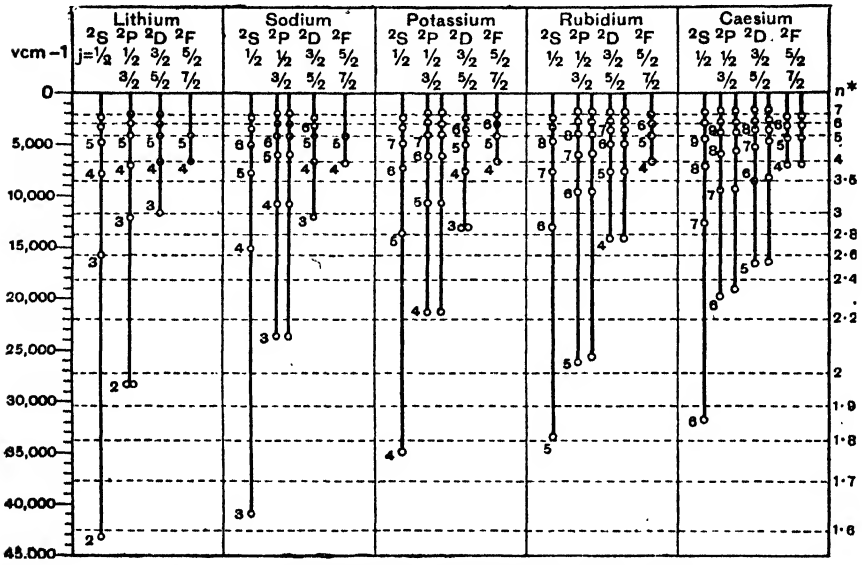


FIG. 158.—Energy levels in spectra of the alkali metals.

The *ions* Ca^+, Sc^{++}, Ti^{+++} and V^{++++} have also one outer electron, or are " hydrogen-like," and the spectra of these " stripped atoms " (Fig. 159) resemble those of the corresponding neutral K atom. With Ca^+ the $4s$ level is lower than the $3d$, but (unlike K) the $4p$ is not. With Sc^{++} the $4s$ and $4p$ levels are higher than the $3d$, so that the next electron after Ca goes into $3d$ rather than $4p$; with Ti^{+++} two, and with V^{++++} three, electrons go into $3d$ levels. (To bring the terms on the same scale, those of Ca^+, Sc^{++}, Ti^{+++} and V^{++++} have been divided by 4, 9, 16 and 25, the squares of the *effective* nuclear charges 2, 3, 4 and 5 (*i.e.* those unscreened by inner electrons).

Calcium has two $4s$ valency electrons. With Sc, owing to the increased nuclear charge, the inner level begins to fill and the electron goes into the $3d$ level. The outer structure of A, 2 | 2 6 | 2 6 |, has begun to fill up towards its maximum of 18, and the Sc structure is 2 | 2 6 | 2 6 1 | 2, derived from that of Ca 2 | 2 6 | 2 6 | 2 by addition of an electron to an inner $3d$ level. This goes on as far as Cr, when one of the two outer $4s$ electrons drops to a $3d$ level, which now contains 5 electrons. These remain in manganese and the next electron goes into the $4s$ level (see Table II, p. 263).

Iron, cobalt and nickel have 6, 7 and 8 electrons, respectively, in $3d$ levels. With copper, another electron drops from the $4s$ level, making $8+10=18$ in the $3s$, $3p$ and $3d$ levels and 1 in the outer $4s$ level. The inner 3-quantum levels now contain the maximum number 18 of electrons allowed by Pauli's principle (Table I). This completed inner group of 18 electrons persists unchanged in all the remaining elements.

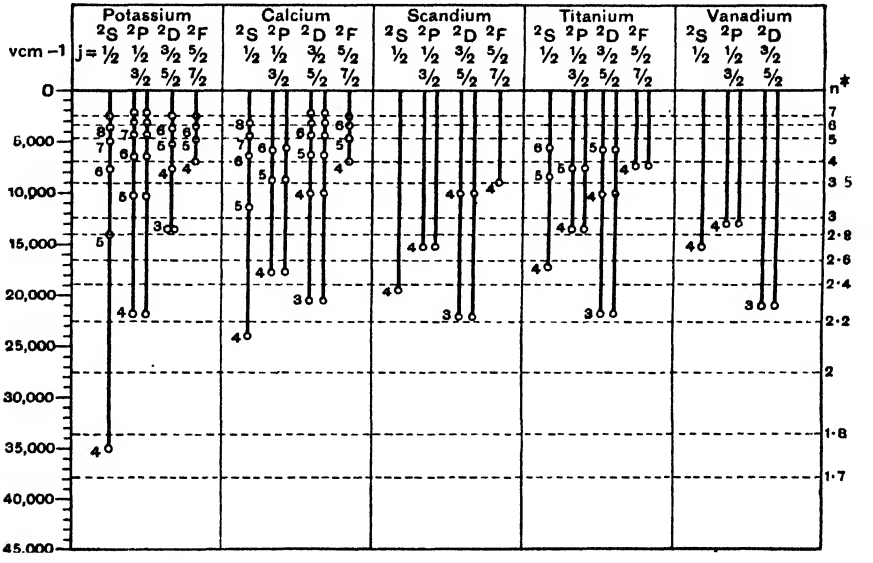


FIG. 159.—Energy levels in spectra of stripped atoms.

The arrangement of electrons in the elements Ti to Cu is required by the spectra and also explains (i) the chemical and physical properties of the elements V, Cr, Mn, Fe, Co and Ni, viz. the arrest of the valency to 2 or its variation by *one* unit at a time (although V, Cr and Mn have very varying valencies, as shown below, these differ by one), (ii) the paramagnetism and (iii) the colour of the ions (supposed to be characteristic of incomplete inner groups), (iv) the changes of direction in the X-ray curves (Fig. 103), and (v) the appearance of the first triad (Fe, Co, Ni).

Element.			Valencies.		
Ti	2	3	4		
V	2	3	4	5	
Cr	2	3		6	
Mn (1)	2	3	4	6	7
Fe (1)	2	3		6	
Co (1)	2	3			
Ni (1)	2	3	4		
Cu 1	2				

This filling up of *incomplete* inner levels was first suggested by Ladenburg (1920) and explained by Bohr.

From copper to krypton the $4s$ and $4p$ levels fill up normally until with krypton they contain $2+6=8$ electrons, and the period is complete.

A new period begins with rubidium, in which a $5s$, loosely bound, electron appears, the $4d$ and $4f$ levels remaining empty. After strontium, with two $5s$ electrons, the next electron goes to a lower $4d$ level in yttrium, and this level is gradually filled, reaching ten electrons in palladium, in which the $5s$ electron drops back. The $5s$ and $5p$ levels are filled up normally to a complete $2+6=8$ group with xenon, which closes the period. In the case of copper all the inner levels, including the $3d$, are filled, but in silver the $4f$ levels are empty.

In the period beginning with caesium a $6s$ electron is added, in barium two $6s$ electrons. From and including lanthanum, however, the valencies remain constant at 3 until the last rare-earth element lutecium is reached, the electrons going to complete the empty $4f$ levels deep inside the atom. To the eighteen electrons of levels of principal quantum number 4 there are now added in succession fourteen more, making up a total of 32, the maximum possible for $n=4$. Since all are well within the stable octet completed in xenon they have no appreciable influence on the chemical properties, which remain practically constant, and this explains both the number (15) and chemical properties of the rare-earth elements in this period (sometimes called **lanthanides**, to distinguish them from the total number of rare-earth elements which includes scandium and yttrium in earlier periods). Just as in the fourth and fifth periods, the arrangement of electrons in the rare-earth elements is accompanied by the appearance of coloured ions and paramagnetism.

The element following lutecium cannot be a rare-earth element but must be a fourth group element related to zirconium. This was confirmed by the properties of hafnium, discovered by Coster and Hevesy.

In the following elements as far as gold, the $5s$ and $5p$ levels of xenon, containing 8 electrons, are completed by the addition of ten electrons to the $5d$ levels, making up a total of 18, whilst with gold the $n=6$ levels begin to fill up, leading to the completion of the $6s$ and $6p$ levels with $2+6=8$ electrons, forming the outer shell of the inert emanation. In the remaining fragmentary period, after a missing element in the first group, the $7s$ level in radium has two electrons. The $6d$ levels begin to fill up with actinium, but when four electrons have occupied $6d$ levels we reach, for some reason not known, the end of the elements with uranium.

If we look back over this view of the Periodic System we notice that each period is characterised by a principal quantum number n of the outer electrons, n being equal to the number of the period. The electrons are arranged in groups or shells, each fully occupied when it contains $2n^2$ (2, 8, 18 or 32) electrons. These groups are divided into sub-groups, defined by the serial quantum number l, the number (2, 6, 10, or 14, for $l=0$, 1, 2, or 3) in each complete sub-group being $2(2l+1)$.

This arrangement, introduced by Stoner (*Phil. Mag.*, 1924, **48**, 719) from the number of Zeeman terms into which the spectrum terms are split by a magnetic field, and by Bury (*J.A.C.S.*, 1921, **43**, 1602) and Main Smith (*J.S.C.I.*, 1924, **43**, 323) on chemical grounds, is required by Pauli's principle.

TABLE II

Valency

Heitler and London (1927) explained the formation of an *electron-pair bond* (p. 210) as due to the interaction of two electrons, one on each atom, having opposite spins ($s = +\frac{1}{2}$ and $s = -\frac{1}{2}$). It is an *exchange* or *resonance effect*, which is explained later (p. 267). Two electrons with identical quantum numbers n, l and m_l but opposite spin quantum numbers $s = \pm\frac{1}{2}$ may form a bond, and *the valency of an atom is equal to the number of unpaired electrons in the outer shell.* The resultant spin $S = \Sigma s$ gives the spin due to unpaired electrons, each contributing $\frac{1}{2}$ unit, hence the *valency* is

$$V = 2S = \text{no. of unpaired electrons.}$$

Each valency bond formed from *two* unpaired electrons decreases S by one unit, hence V decreases in multiples of two, and it is commonly found that the valencies differ by 2 or a multiple of 2, as is seen from Table III. The + sign denotes loss or sharing of electrons, the − sign gain of electrons.

Table III. Variable Valencies

Group.	Element.					Valencies.			
	$n=2$	3	4	5	6				
VII	(F)	Cl	Br	I	—	−1	+3	+5	+7
VI	(O)	S	Se	Te	(Po)	−2	2	4	6
V	N	P	As	Sb	Bi			3	5
IV	C	Si	Ge	Sn	Pb			2	4
III	(B)	(Al)	(Ga)	In	Tl			1	3

Table IV gives the results for twelve elements of the first periods. The figures in the table give the numbers of electrons with the given quantum numbers, and the valency V is equal to the number of unpaired electrons (which can pair with electrons of opposite spins of other atoms), *i.e.* the sum of the values of 1 in the table, values of 2 denoting paired electrons. Bivalent and quadrivalent carbon are both possible; nitrogen has a covalency of 3 only, fluorine only of 1, and oxygen only of 2, whilst phosphorus can have valencies of 3 and 5, chlorine of 1, 3, 5 and 7, and sulphur of 2, 4 and 6.

Some elements, particularly heavier elements of the *b* sub-groups of the periodic table (p. 176), *behave as if two of the valency electrons were not functioning* in some compounds, and thus the element resembles the one which is two places in front of it. Thus, $Tl^{\cdot}$ is like $Au^{\cdot}$, $Pb^{\cdot\cdot}$ like $Hg^{\cdot\cdot}$, and ICl_3 and IF_5 are like $SbCl_5$ and $SbCl_5$. This **inert pair** of electrons appears in monatomic cations and in covalent compounds; in the cations it may exist as an outer group, *e.g.* in $Sn^{\cdot\cdot}$ or $Tl^{\cdot}$; in the covalent compounds a "mixed" group of electrons (shared + unshared) does not normally exceed 8, whilst wholly shared groups up to 16 are known, *e.g.* in OsF_8. But if the atom has an inert pair the valency group is abnormal; it can be reduced to a normal form (octet or wholly shared group)

TABLE IV. COVALENCIES

n	1	2		n	1	2		3		
l	0	0	1	l	0	0	1	0	1	2
m_l	0	0	−1 0 1	m_l	0	0	−1 0 1	0	−1 0 1	−2 −1 0 1 2
H	1			P	2	2	2 2 2	2	1 1 1	
He	2				2	2	2 2 2	1	1 1 1	1
Li	2	1		S	2	2	2 2 2	2	2 1 1	
Be	2	1	1		2	2	2 2 2	2	1 1 1	1
B	2	2	1							
	2	1	1 1		2	2	2 2 2	1	1 1 1	1 1
C	2	2	1 1	Cl	2	2	2 2 2	2	2 2 1	
	2	1	1 1 1							
N	2	2	1 1 1		2	2	2 2 2	2	2 1 1	1
O	2	2	2 1 1		2	2	2 2 2	2	1 1 1	1 1
F	2	2	2 2 1		2	2	2 2 2	1	1 1 1	1 1 1

by transferring two unshared electrons from the valency group to the core. If the shared electrons are shown in heavy figures we have, *e.g.* $SbCl_3$ **2 . 6**, viz.

Cl
..
: Sb : Cl : and SbF_5 **10**, which have normal valency groups ; and ICl_3 **4 . 6** and IF_5
..
Cl

2 . 10, which are abnormal but can be reduced to normal groups by assuming that two unshared electrons are part of the atomic core. The effect of the inert pair is to diminish the ion valency by 2 and increase the covalency by 2 (Sidgwick, *Ann. Rep. C. S.*, 1933, 120).

WAVE MECHANICS

It was mentioned on p. 255 that the details of Bohr's theory of atomic structure which postulate electrons as point charges revolving in orbits around the nucleus have been abandoned for reasons which need not be stated. The explanation of the structure of the periodic table on pp. 259–263 is still valid, as it depends only on Pauli's principle and on energy levels of electrons which are spectroscopic data.

The modern theory of atomic structure is based on *the wave nature of the electron*. Electrons in motion behave as if they were associated with charac-

teristic waves, the lengths of which are given by a formula due to de Broglie (1924):

$$\lambda = \mathbf{h}/mv,$$

where **h** is Planck's constant and m and v are the mass and velocity of the electron. Beams of electrons are diffracted by matter, *e.g.* by reflection from a crystal or in passing through a thin metal foil, in the same way as X-rays (Davisson and Germer, 1927; G. P. Thomson, 1927). This dual aspect of an electron, particle or wave, is analogous to the dual character of light, which sometimes behaves as if it consisted of corpuscles or *photons* (*e.g.* in the photo-electric effect when electrons are expelled from metals by ultra-violet light) and sometimes as if it consisted of waves, which give rise to interference and diffraction.

Schrödinger (1926) supposed that the charge of the electron is not concentrated in a particle but extends in space as a kind of "cloud," the density of which is proportional to ψ^2, where ψ is a *wave function*, whilst Born (1926) suggested that ψ^2 gives the probability of the occurrence of the electron, considered as a particle, in any given part of space. Schrödinger showed that an equation involving ψ and E, the energy of the electron in an atom, has satisfactory solutions only when E has a series of definite values. For the hydrogen atom these are shown to be the same as the values given by Bohr's equations (1) and (2), p. 256, so that the quantum number n appears without any special assumption of non-radiating orbits. The wave function ψ now replaces Bohr's electron orbits.

Bond formation.—If the wave functions of two electrons 1 and 2 associated with two hydrogen nuclei a and b respectively are $\psi_a(1)$ and $\psi_b(2)$, the two possible states of the H_2 molecule are represented by the products $\psi_a(1)\psi_b(2) = A$ and $\psi_a(2)\psi_b(1) = B$, since the two electrons are indistinguishable according to the wave theory. The *orbital part of the wave function* of H_2 will be one of the linear combinations given approximately by:

$$\Psi_S = (A + B)/\sqrt{2} \quad \text{and} \quad \Psi_A = (A - B)/\sqrt{2},$$

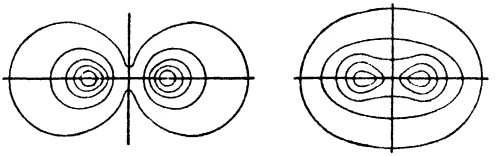
for positions between the nuclei (*i.e.* small distances), $1/\sqrt{2}$ being the approximate normalising factor ensuring that the total probability of the existence of an electron in the whole of space is unity.

The probability of the occurrence of an electron between the nuclei is proportional to Ψ^2, where:

$$\Psi_S^2 = (A^2 + B^2 + 2AB)/2 \quad \text{and} \quad \Psi_A^2 = (A^2 + B^2 - 2AB)/2.$$

Thus $\Psi_S^2 > \Psi_A^2$, so that the electron density (corresponding with capacity for bond formation) is greater for the symmetrical function, since A and B are positive. This is shown in Fig. 160, in which contour lines of the electron density are plotted round the nuclei: (*a*) represents Ψ_A^2 and (*b*) Ψ_S^2. Thus ***the symmetrical orbital wave function corresponds with bonding properties and the anti-symmetrical orbital function with anti-bonding properties of the electrons.***

Pauli's principle (p. 257) in its wave-mechanical aspect implies that *the complete wave function of an atomic or molecular system cannot be symmetrical in respect of similar particles* (*electrons or nuclei*). The complete wave function



(a) (b)

FIG. 160.—Contour lines of electron density in hydrogen molecule.

is the product of the orbital function Ψ_S or Ψ_A and the spin function. The *spin function* is S_S when the electron spins are parallel, and S_A when they are anti-parallel ($+\frac{1}{2}$ and $-\frac{1}{2}$). S_S is symmetrical because its sign is unchanged when the electrons are interchanged, and S_A is anti-symmetrical, since its sign is changed.

The four possible complete wave functions are :

$$\Psi_S S_S \qquad \Psi_S S_A \qquad \Psi_A S_S \qquad \Psi_A S_A,$$

but Pauli's principle excludes the first and fourth. Since a hydrogen molecule can be formed only when the orbital function is symmetrical (Ψ_S), the third case is also excluded, and hence the two hydrogen atoms can combine only when the complete wave function is given by the second expression, *i.e.* when the spin function is S_A, when *the two electrons have anti-parallel spins*, and the resultant electron spin of the stable molecule is $+\frac{1}{2}-\frac{1}{2}=0$. The chemical bond is thus interpreted as a pair of electrons with opposite spins ($\rightleftarrows$). This is the theory of bond formation given by Heitler and London (p. 264), which has, therefore, a theoretical basis in wave mechanics (Penney, *The Quantum Theory of Valency*, 1935 ; Rice, *Electronic Structure and Chemical Binding*, New York, 1940 ; Sutton, *J.C.S.*, 1940, 544).

This theory is capable of giving a very simple explanation of the existence of *directed bonds* (Pauling, *J.A.C.S.*, 1931, **53**, 1367 ; *The Nature of the Chemical Bond*, New York, 1940 ; Van Vleck and Sherman, *Reviews of Modern Physics*, 1935, **7**, 167 ; Mills, *J.C.S.*, 1942, 457). The wave function of an *s*-electron, *i.e.* (p. 258) one for which $l=0$, is a sphere. The *p*-electrons (for which $l=1$) have wave functions which have axial distributions at right angles, and these give rise to directed bonds. A bond is formed by the overlapping of regions in which the wave functions (or electron densities, proportional to ψ^2) have pronounced values.

We can thus represent the *s*-electron of a hydrogen atom by a sphere and combination of two hydrogen atoms by overlapping spheres (corresponding with increased electron density), the spins of the two electrons being anti-parallel. The bond strength for an *s*-electron is represented by 1.

Oxygen has four *p*-electrons ($l=1$), but these are in different states according to an empirical *rule of maximum multiplicity*, which says that *when electrons are added successively, as many orbits are singly occupied as possible before any*

pairing of electron spins occurs. There are three p-orbits with wave functions p_x, p_y, p_z directed along three axes x, y, z at right angles, and the electron densities are dumb-bell shaped (Fig. 161) when the orbits are occupied by

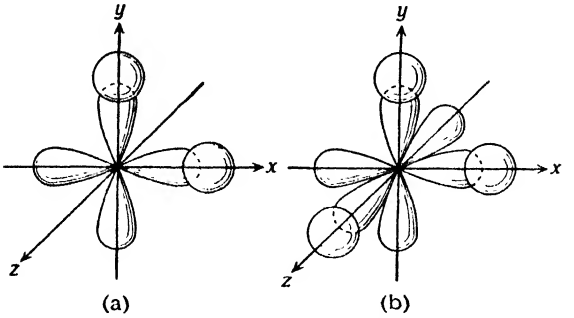


FIG. 161.—Formation of directed bonds.

electrons. The bond strength is represented by $\sqrt{3}$. Of the four p-electrons, two go singly into two orbits, according to the rule, but the other two electrons are forced to go together, with anti-parallel spins, into the remaining orbit. Thus two unpaired valency electrons are available to combine with two s-electrons of opposite spins of two hydrogen atoms to form H_2O. Another rule states that *a bond is formed by the maximum overlapping of wave functions.* Hence the hydrogen atoms must approach along the two directions of the axes of the wave functions of the two valency p-electrons of the oxygen, which are at right angles, and the H_2O molecule formed is shown in Fig. 161*a*. Owing to repulsion of the two hydrogens the angle is greater than 90°, probably 106°, but in H_2S the angle is practically 90°. This type of binding is called sp^2s.

Nitrogen has three p-electrons and these can occupy singly the p_x, p_y and p_z orbits, and combine with the s-electrons of three hydrogen atoms, forming a molecule NH_3 with the three bonds at right angles, and with p^3s^3 binding (Fig. 161*b*).

The normal carbon atom $1s^22s^22p^2$ has only *two* p-electrons, and we might expect a compound CH_2, since the spins would be unpaired and would combine with anti-parallel spins of two s-electrons, one in each hydrogen atom. To exert four valencies *one* of the $2s$-electrons ($n=2$, $l=0$) must be excited and pass from its normal s-state to a $2p$-state, when the atom becomes $1s^22s2p^3$ with *four* unpaired spins. The directions of these valencies might be supposed to be one undirected, and three at right angles (p_x, p_y and p_z) as in nitrogen. When, however, the bond energy greatly exceeds the excitation energy for raising an electron from an s- to a p-level, the quantisation changes and s- and p-electrons assume equivalent wave functions of strength 2 directed towards the four corners of a regular tetrahedron, so that CH_4 is formed as a tetrahedral molecule. This process is called ***s-p-hybridisation***, since the actual wave functions of the bonds are formed by combining s- and p-functions to form stronger bonds than either separately.

The nitrogen in NH_4^+ has one *s*- and three *p*-electrons, so that conditions for hybridisation occur and the ion is tetrahedral. In NH_3 and R_3N (amines) the molecule is also supposed by Pauling to approach a tetrahedral shape, the unshared pair occupying the fourth corner.

It is only possible to regard a single electron as having bonding properties when the potential field of the two atoms is approximately symmetrical, and in this case *exchange energy* leads to binding by one electron (*single electron bond*) holding two nuclei together by first belonging to one nucleus and then to the other, because the two electronic states

$$A \cdot B \quad \text{and} \quad A \cdot B$$

have nearly equal energies. This is a rather special example of what is called *resonance*. The boron hydrides (p. 406) are probably the only stable neutral molecules in which a single electron bond is significant.

Resonance.—The name *resonance* is given by Pauling (1933) to a state in which *the electronic configuration of a molecule can be represented in two or more ways, subject to the conditions that*: (i) *the positions of the atoms remain approximately unchanged*, (ii) *the energies of the various states are not very different*, (iii) *the structures have the same number* (including zero) *of unpaired electrons* (see Sidgwick, *J.C.S.*, 1936, 533; 1937, 694; Pauling, *The Nature of the Chemical Bond*, 1940).

An important result which follows from quantum mechanics is that *the potential energy of the molecule is lower when it is in a state comprising the various possible separate electronic configurations than its value for any one of the latter*, so that *resonance confers stability*. In addition, there is often a shortening of interatomic distances in the bonds in which resonance occurs, although this effect is less important than was once thought.

The actual state is not a mixture of molecules each in one of the separate states, but rather there is a levelling out of the electron density so that each individual molecule is in the state comprising all the separate possible states to some extent. Where resonance is between a single and a double bond, the actual bond is to be regarded as one bond having some single bond character and some double bond character, and often more of one than the other.

A molecule in which there is resonance is not so much in a bond state *intermediate* between two (or more) states (for which the name "mesomerism" obviously might be and has been proposed), but is in a quite *special* state involving an increased stability, and so differing from any of those partial states into which the actual one might, at first sight, seem capable of dissection. The actual state may, *e.g.*, be closer to one of these than to the other (or others).

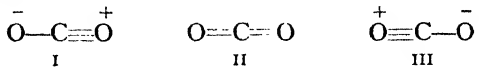
The formula of *carbon dioxide* could be written as:

$$\underset{\text{I}}{:\ddot{O}:C:::O:} \qquad \underset{\text{II}}{:\ddot{O}::C::\ddot{O}:} \qquad \underset{\text{III}}{:O:::C:\ddot{O}:}$$

and for each the O to O distance should be about 2·44 A. and the heat of formation (evolved) from the atoms about 350 k. cal. per mol. The observed values are 2·32 A. (Houston and Lewis, 1931) and 380 k. cal., which indicate

that the actual state of the molecule is a *resonance hybrid* among the three forms. The difference $380 - 350 = 30$ k. cal. is the *resonance energy*, and the energy of the hybrid is *smaller* by this amount *than the energy of any single form.*

Forms I and III involve electron transfer from form II and are ionic types, whilst II is covalent:

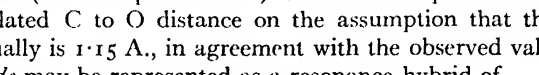


I II III

Since I and III are equivalent they are represented by equal amounts in the hybrid, and since the directions of polarity are opposite the hybrid molecule is non-polar, agreeing with the zero electric moment (p. 276). When the limiting forms have large but opposed dipole moments, the effect of resonance is to diminish or even (as in the present case) to annul the dipole moment.

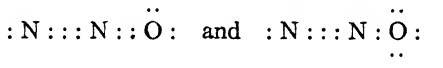
The calculated C to O distance on the assumption that the three forms contribute equally is 1·15 A., in agreement with the observed value.

Nitric oxide may be represented as a resonance hybrid of

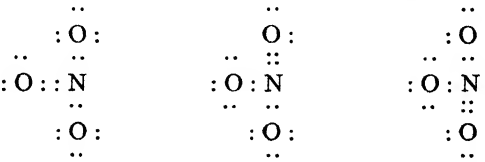


with perhaps some contribution of  , and as the gas has a small but definite electric moment of 0·16 D. the ionic forms (I) and (III) do not contribute quite equally. (A *mixture* of the two forms as separate molecules would have a high moment.) The odd electron is not here located on either N or O, but on an orbit of the whole molecule.

Nitrous oxide is regarded as a resonance hybrid of:



The acid radicals NO_3', CO_3'' and SO_4'' are found by crystal structure measurements to be completely symmetrical, all the oxygen atoms being equivalent, so that there must be complete resonance resulting in the double bond being equally shared with all the oxygen atoms, *e.g.*:



Cases such as the resonance of the two forms of nitric oxide, where an odd electron is involved, are regarded by Pauling as examples of a *three electron bond, i.e.* resonance between  and  , and represented, *e.g.* as  , and the oxygen molecule (which is paramagnetic and hence cannot have the structure ) as  , with two such bonds. These formulae obviously violate the octet rule, since in the NO molecule each atom is sur-

rounded by nine electrons, and in the O_2 molecule by ten, but this rule is also violated in some more ordinary molecules, *e.g* SF_6.

Magnetic Moments of Ions

The *moment* of a bar magnet is the pole strength m multiplied by the distance l between the poles: $\mu = ml$. A rotating electron, and an electron revolving in an orbit, are equivalent to circular currents and hence set up magnetic moments. The first depends on the spin (quantum no. s) and the second on the orbital revolution (quantum no. l). The moment due to the revolution of an electron in the smallest Bohr orbit ($n = 1$) of the hydrogen atom (p. 257) is taken as the unit of atomic magnetic moment and is called a *Bohr magneton*. An equation representing the magnetic moment (in Bohr magneton units) of *paramagnetic ions of the transition metals* (p. 261) is:

$$\mu_B = \sqrt{4S(S+1) + L(L+1)},$$

in which S is the resultant spin ($2S$ is the number of *unpaired* electrons, each with spin $\frac{1}{2}$) and L is the resultant orbital angular momentum (formed from the l values). Except with cobalt, the interaction and perturbing effects of other ions in the solution or crystal cancel out most of the L-contribution (since the incomplete $3d$ shell is outermost) and only the electron spin need be considered (Bose, 1927; Stoner, 1929; Pauling, *J.A.C.S.*, 1931, **53**, 1392):

$$\therefore \mu_B = 2\sqrt{S(S+1)}.$$

If the number of unpaired electrons is n, then $S = \frac{1}{2}n$:

$$\therefore \mu_B = \sqrt{n(n+2)}.$$

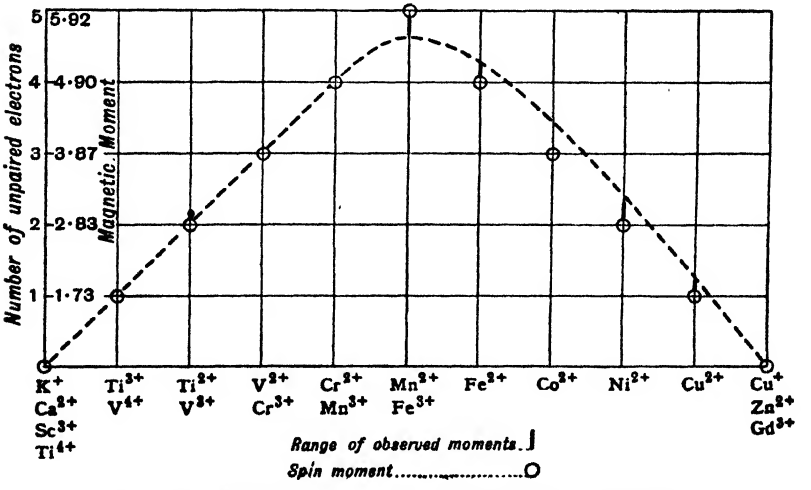


FIG. 162.—Magnetic moments of ions (in Bohr magnetons).

Fig. 162 shows that μ_B calculated from the last equation for simple salts and oxides is in good agreement with experiment. In complex compounds (*e.g.*

cobaltammines) the electronic levels are rearranged and the resulting ion may be diamagnetic. In the case of rare-earth ions the incomplete shell is $4f$, and as this is screened by the $5p$ and $5s$ shells outside it, the moment is no longer accounted for by S alone.

The rule of maximum multiplicity (p. 267) requires the $3d$ electrons to remain unpaired until they are forced to share orbitals, which occurs when the five $3d$ orbitals are occupied, a sixth electron then sharing an orbital with another. The spin moment thus rises to a maximum of

$$\sqrt{n(n+2)} = \sqrt{5 \times 7} = 5{\cdot}92,$$

and then falls. This is shown in the table (Pauling), in which the first column of numbers gives the number of $3d$ electrons :

TABLE V

		n	$\mu_B$calc.	$\mu_B$obs.			n	$\mu_B$calc.	$\mu_B$obs.
K^+, Ca^{++}, Sc^{3+}, Ti^{4+}	0	0	0·00	0·00	Fe^{++}	6	4	4·90	5·3
V^{4+}	1	1	1·73	1·7	Co^{++}	7	3	3·88	5·0–5·2
V^{3+}	2	2	2·83	2·4	Ni^{++}	8	2	2·83	3·2
V^{++}, Cr^{3+}	3	3	3·88	3·8–3·9	Cu^{++}	9	1	1·73	1·9–2·0
Cr^{++}, Mn^{3+}	4	4	4·90	4·8–4·9	Cu^{+}, Zn^{++}	10	0	0·00	0·00
Mn^{++}, Fe^{3+}	5	5	5·92	5·9					

The larger values in the last column may be due to contributions from the orbital (L) moments of the electrons.

COORDINATION COMPOUNDS

In the application of Pauling's theory of bond formation (p. 267) to elements of higher atomic number, such as occur in many *coordination compounds* (p. 213), it is necessary to take account of the d- electrons ($l = 2$) as well as s- and p-electrons (Pauling, *J.A.C.S.*, 1932, **54**, 988).

If one d-electron is available, then four equivalent bonds can be formed with one s- and two p-electrons, the normal quantisation being broken down and hybridisation taking place with the formation of equivalent orbits (p. 268). The maximum wave functions (2·694) are in this case at right angles to one another in a plane ; a fifth possible bond not in the plane would be weak (1·732). This planar structure is known (from X-ray and other data) in the cases of $Ni(CN)_4''$, $PtCl_4''$, $PdCl_4''$, $AuCl_4'$, and nickel glyoximes (p. 216). Although the metals give paramagnetic cations, *e.g.* $Ni^{\cdot\cdot}$, the complex ions are diamagnetic because the change in quantisation produces closed configurations of electrons.

In general, 4-covalent atoms form valency bonds from two outermost s and p sub-groups, and these bonds are arranged tetrahedrally (p. 268) ; but when one or more electrons come from an inner d sub-group hybridisation may form a planar arrangement of bonds. Since the magnetic properties depend mainly on the d-electrons, their sharing with other electrons to form bonds will reduce the

paramagnetic moment, which may become diamagnetic, as in the case of nickel forming planar glyoximes.

When two *d*-electrons with unpaired spins are available, six bonds can be formed by hybridisation with one *s*- and three *p*-electrons. These six bonds, of maximum value 2·923, are directed towards the corners of a regular octahedron. This is the structure of $Co(NH_3)_6'''$, $PtCl_6''$, $Fe(CN)_6'''$, etc.

When three *d*-electrons with unpaired spins hybridise with one *s*- (or three *p*- and one *s*-), four equivalent bonds of strength 2·95 arranged tetrahedrally result. This is probably the arrangement with CrO_4'', MoO_4'', $Zn(CN)_4''$, $Cd(CN)_4''$, $Hg(CN)_4''$, the last three of which are proved to be tetrahedral by X-ray analysis, and the elements Zn, Cd and Hg each have two *d*-electrons more than Ni, Pd and Pt, respectively, which form planar structures.

In Fig. 163 the ferrous ion is shown in row I with its four unpaired 3*d*-electrons in circles (2) to (5). If these are paired in the levels (2) and (3), as shown in

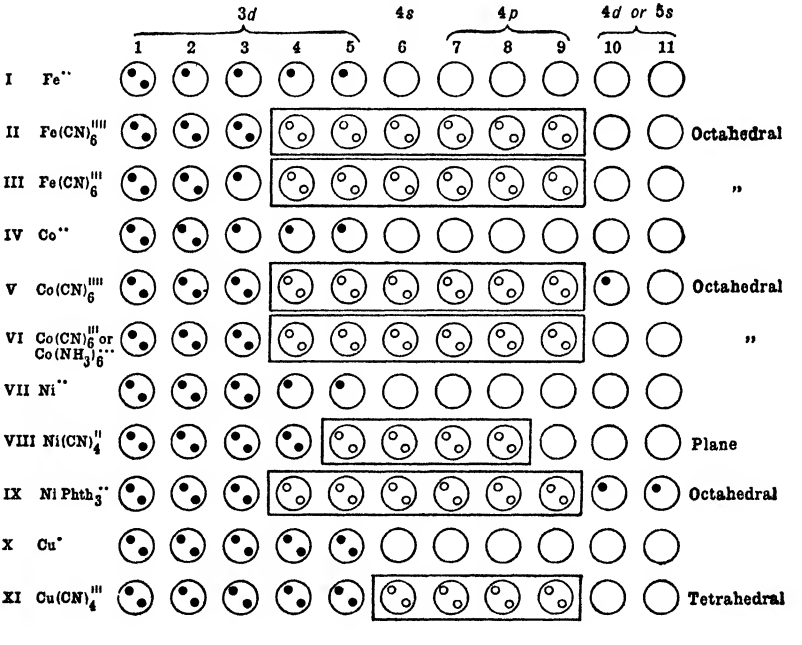


FIG. 163.—Bond types in coordination compounds.

row II, two new *d*-orbits (4) and (5) become available for combination with 4*s*- and 4*p*-orbits and six new octahedral bonds can be formed, so giving rise to a completely closed configuration as shown in row II; thus the ion $Fe(CN)_6''''$

for example is diamagnetic. Since the ferric ion has only three unpaired 3*d*-electrons in orbits (2), (3) and (4), the complex ion $Fe(CN)_6'''$ formed by pairing off two of these will have an odd electron (shown in orbit (3) in row III) and is paramagnetic.

With bivalent cobalt one electron in orbit (5) in row IV is promoted to a 5*s*-level in orbit (10) in row V and is readily removed by oxidation, so that $Co(CN)_6''''$ is a powerful reducing agent, passing into $Co(CN)_6'''$ as shown in row VI. Similarly $Co(NH_3)_6^{++}$ readily oxidises to $Co(NH_3)_6^{+++}$.

By the pairing of *d*-levels in Ni^{++} in rows VII–VIII an orbit (5) is made available for the formation of a planar diamagnetic complex. Coordination with three 2-coordinating groups causes promotion of two electrons from orbits (4) and (5) in row VII to orbits (10) and (11) in row IX and the formation of a paramagnetic octahedral complex.

The Cu^+ (also the Zn^{++}) ion has completed 3*d* levels in row X and can hybridise only in 4*s* and 4*p* orbits, forming tetrahedral diamagnetic 4-coordination complexes in row XI. Since the nickel *atom* in the $3d^{10}$ state is isoelectronic with Cu^+, $Ni(CO)_4$ is isoelectronic with $Cu(CN)_4'''$, has a tetrahedral configuration, and is diamagnetic.

The 3*d* level in Cr^{6+} is empty and the lowest orbits with which hybridisation can occur are 3*d* and 4*s*; $[sd^3]$ hybridisation occurs and 6-valent chromium compounds, such as CrO_4'', have the tetrahedral configuration.

In Fe^{3+} the five 3*d* electrons are unpaired in separate orbitals and the magnetic moment is $\mu_B = 5{\cdot}92$ (p. 272), but in an octahedral ferric complex in which the central atom forms six d^2sp^3 bonds with surrounding groups, only three 3*d*-orbitals are available for the five unshared 3*d*-electrons, which must thus form two pairs and the remaining unpaired 3*d*-electron gives the small moment of $\mu_B = 1{\cdot}73$. The observed value for $K_3Fe^{III}(CN)_6$ is 2·33, the excess being probably due to the contribution of orbital (*L*) moment (p. 272).

Sizes and Shapes of Molecules

Several methods provide quantitative information about: (i) the distances between the centres of atoms in molecules (or ions in crystal lattices), (ii) the modes of arrangement of these atoms, and (iii) the angles between the valency bonds linking the atoms together (Glasstone, *Recent Advances in Physical Chemistry*, and *Recent Advances in General Chemistry*; Sidgwick and Bowen, *Ann. Rep. C.S.*, 1931, 367). These results confirm those found qualitatively from chemical considerations. The most important methods are:

1. *Diffraction of X-rays and of electrons* by solids, liquids, and gases.
2. *Spectroscopic methods*, including Raman, infra-red, and visible band spectra.
3. *Electric dipole moments.*
4. *Magnetic susceptibility.*

X-ray methods.—The *X-ray method* as applied to crystals has been described (p. 238). It has also been used to investigate the so-called "amorphous solids" (*e.g.* glasses), liquids and even gases and vapours. The "powder method" (p. 239) often gives diffraction patterns in these cases, indicating some regularity in molecular arrangement of liquids and of atomic structure in

gases. Liquid water and mercury show characteristic spacings, and the structure of water has been deduced from the results (p. 674). Glass seems to consist of minute crystals (size 10^{-6} to 10^{-7} cm.) with a random arrangement. Plastic sulphur has a fibrous structure composed of long chains of sulphur atoms (see p. 692). The diffraction of X-rays by gases (Debye and Ehrenfest, 1915) has been used in the determination of interatomic distances, but has been superseded by the electron diffraction method, with which a much shorter exposure is required.

Electron diffraction.—The *electron diffraction method* depends on the wave nature of the electron (p. 265), beams of which are diffracted like X-rays by matter (Brockway, *Reviews of Modern Physics*, 1936, **8**, 231 ; *Ann. Rep. C.S.*, 1936, 65). This method has shown that the molecules $HgCl_2$, $HgBr_2$, HgI_2, C_2N_2, CS_2 and C_3O_2 are linear ; BCl_3 is planar and triangular ; $SiCl_4$, $GeCl_4$, $TiCl_4$, $Ni(CO)_4$ and P_4 are tetrahedral ; PCl_5 is a trigonal bipyramid ; SF_6 is octahedral ; PF_3 is pyramidal ; and F_2O, Cl_2O and SO_2 are bent at angles of 100°, 115° and 120°, respectively. The interatomic (" bond ") distances were found to vary from about 1·5 to 2·5 A.

The bond distance is important in deciding the bond character and the presence of resonance (p. 269). The distances between the centres of atoms joined by covalencies are regulated by the so-called *normal covalency radii* of atoms, the length of the bond being the sum of the valency radii of the two atoms it joins (Pauling, *The Nature of the Chemical Bond*, 1940, 164, 179).

For *single bonds* the radii (in A.) have been given as : H 0·30 ; B 0·88 ; C 0·771, Si 1·17, Ge 1·22, Sn 1·40, Pb 1·46 ; N 0·70, P 1·10, As 1·18, Sb 1·36, Bi 1·46 ; O 0·73, S 1·04, Se 1·14, Te 1·32 ; F 0·64 (0·71 in F_2), Cl 0·99, Br 1·11, I 1·28 ; Be 1·06, Mg 1·40, Zn 1·31, Cd 1·48, Hg 1·48. For *doubly linked* atoms they are : C 0·67, N 0·60, O 0·57, P 1·00, S 0·94, and for *trebly linked* atoms : C 0·60, N 0·55, O 0·50, P 0·93, S 0·87. In some cases (SF_6, etc.) the calculated additive value is somewhat larger than the observed, which may indicate a tendency for covalent to pass into electrovalent links (p. 244), and more accurate measurements (Schomaker and Stevenson, *J.A.C.S.*, 1941, **63**, 37) show that the rule of the additivity of covalent radii is not exact, the influence of even a small electrovalent component in the bond being quite large.

Optical methods.—The *infra-red absorption spectra* give information on the moments of inertia and hence the interatomic distances in the case of molecules having electric moments (p. 276). In this way the following results were found for interatomic distances (in A.) in diatomic molecules : HF 0·923, HCl 1·281, HBr 1·420, HI 1·617. Isotopic molecules (*e.g.* $H^{35}Cl$ and $H^{37}Cl$) have different moments of inertia and hence are detected in band spectra.

More accurate results are obtained by so-called *rotation-vibration spectra*, and absorption spectra in the *visible spectrum*, due to electronic motions, are applicable in the case of molecules without permanent electric moments.

The following interatomic distances in A. were found for polyatomic molecules : CO_2 C to O 1·16 ; C_2H_2 C to C 1·30 C to H 1·06 ; CH_4 C to H 1·11 H to H 1·81 ; NH_3 N to H 1·02 H to H 1·64 ; H_2O O to H 1·01 H to H 1·91 ; H_2S S to H 1·35 H to H 2·24.

In light scattered from a transparent liquid or solid, extra lines with a small frequency difference appear alongside the line due to the incident monochromatic light. From observations of these *Raman spectra* the vibrational frequencies of pairs of atoms in the molecule are found, and by assuming that the particles execute approximately simple harmonic vibrations, the *restoring forces* for unit displacement may be calculated. These may be regarded as measuring the bond strengths.

An interesting result is found with single, double and triple bonds between carbon atoms, for which the restoring forces, in dynes $\times 10^{-4}$ are: C—C 2·08 C=C 4·20 C≡C 6·32, which are *approximately* in the ratio 1 : 2 : 3, the force being proportional to the number of valency bonds. This holds approximately also for other atoms similarly linked, whether they are the same or different (*e.g.* C=O, O=O, and whether the bond is an ordinary covalency or a coordinate bond (p. 213), N≡N, C≡O.

An important quantity which can be accurately calculated from spectroscopic results is the *heat of dissociation* of a diatomic molecule into its atoms.

The electronic vibrational band spectrum consists of a number of groups of lines which crowd together in the direction of increasing frequency and then pass over into a continuous spectrum. The band structure is due to the vibration of the atoms in the molecule. When the vibrational energy, which increases with the frequency, is so large that the atoms fly apart, their motion is no longer quantised and a continuous spectrum results. The frequency ν where the continuum commences thus gives the energy $h\nu$ required to dissociate the molecule and, after correction if one or both atoms are in excited states, the heat of dissociation into normal atoms is found.

The heats of dissociation (absorbed) of some diatomic molecules into atoms, and triatomic molecules into radicals, are given in the table in k. cal. per mol.

TABLE VI. HEATS OF DISSOCIATION

H_2	103	I_2	36	CO_2 (CO + O)	125·8
HD	103·5	HF	140	N_2O (NO + N)	88·5
D_2	104·5	HCl	102	H_2O (HO + H)	118
O_2	117	HBr	86	NO_2 (NO + O)	77
NO	123	HI	66		
N_2	170	S_2	102		
Cl_2	57	P_2	120		
Br_2	46	C_2	127		

From these, the heats of formation of compounds from the *atoms* may be calculated. *E.g.* $H_2 + \frac{1}{2}O_2 = H_2O$ (gas) + 68·5 k. cal. (evolved);

$$\therefore (2H - 103) + (O - 58{\cdot}5) = H_2O \text{ (gas)} + 68{\cdot}5;$$
$$\therefore 2H + O = H_2O \text{ (gas)} + 230 \text{ k. cal. (evolved).}$$

Electric dipole moments.—Many covalent molecules possess a *permanent electric dipole*, the strength of which is expressed as the *electric dipole moment*, μ.

A dipole moment will be produced by an *unequal sharing*, on the average, of the electrons forming the bond between two atoms. In the HCl molecule, on the average, the valency electrons spend more time near the chlorine nucleus, with its larger positive charge, than near the hydrogen nucleus. The molecule thus behaves as if the chlorine end were negative and the hydrogen end positive, and this may be represented by the symbol $\overset{+\rightarrow}{\mathrm{HCl}}$, where the point of the arrow shows the negative end and the cross the positive end. The actual location and strength of the charges is not known, but only the product of charge and distance, which is the electric moment.

The electric moments give useful information about the shapes of molecules. The total moment as measured is a vector quantity, since it has magnitude and direction (from the positive to the negative end of the dipole), and it may be calculated by adding the moments of the various atom or radical bonds by vector addition like the parallelogram of forces. In this, suitable bond angles must be assumed to give the correct resultant, and from these angles some idea of the shape of the molecule can obviously be obtained. The results are less precise than those found by X-ray or electron diffraction experiments, but are in agreement with these.

The electric moment of carbon dioxide is zero, hence the three atoms in the molecule must be in line O=C=O, when the two C=O moments (known to exist in other compounds, *e.g.* acetone) cancel. (This result is confirmed by the infra-red spectrum.) Three phosphorus halides have moments (in c.g.s. units $\times 10^{18}$): $PCl_3 = 0{\cdot}85$, $PBr_3 = 0{\cdot}61$, $PI_3 = 0$, indicating a pyramidal structure for the first two and a plane structure (with the phosphorus at the centre of an equilateral triangle and the three iodines at the corners) for the third.

Electric moments are very useful in distinguishing *cis-* and *trans*-isomers (p. 220); *hyponitrous acid* HO—N=N—OH, for example, must have the *trans*-configuration, since the two =N—OR moments in its esters cancel, giving an observed moment of practically zero (Hunter and Partington, *J.C.S.*, 1933, 309):

$$\begin{array}{l} \mathrm{N}\overset{+\rightarrow}{}\mathrm{OR} \\ \quad\| \\ \mathrm{RO}\overset{\leftarrow+}{}\mathrm{N} \end{array}$$

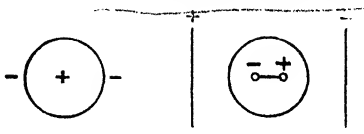
Instead of saying that the polarity of H—Cl is due to the electron pair forming the bond being drawn nearer the electronegative Cl and giving H ... : Cl rather than H : Cl, it is now more usual to say that the actual state of the molecule is a resonance hybrid involving a certain amount of ionic $H^+ Cl^-$ structure as well as covalent structure H : Cl.

The ionic forms will have large electric dipole moments, hence some information about them may be obtained. Carbon dioxide may be a resonance hybrid of three structures:

$$\underset{\text{I}}{:\overset{+}{\mathrm{O}}\equiv\mathrm{C}-\overset{-}{\underset{\cdot\cdot}{\mathrm{O}}}:} \qquad \underset{\text{II}}{:\mathrm{O}=\mathrm{C}=\mathrm{O}:} \qquad \underset{\text{III}}{:\overset{-}{\mathrm{O}}-\mathrm{C}\equiv\overset{+}{\mathrm{O}}:}$$

The first and third would correspond with large equal moments in opposite

directions, and since the total moment is zero they must contribute equally by resonance to the actual state of the molecule (p. 270).



a *b*

FIG. 164.—Deformation of charges to produce an induced dipole.

Molecules with or without a permanent dipole acquire an *induced dipole* under the influence of an electric field and in the direction of this field. In this case the electron shell of an atom is displaced relative to the positive core, and the result is equivalent to the formation of a positive and negative doublet (Fig. 164). This is stronger the more polarisable the atom, molecule or ion, and the effect, which can be measured from the refractive index, also enables ionic radii to be calculated.

Magnetism.—The *magnetic susceptibility* of a substance can give valuable information as to molecular structure. A general rule is that *molecules containing only pairs of electrons with anti-parallel spins are diamagnetic, whilst molecules and free radicals containing unpaired electrons are paramagnetic.*

Thus H : H, H : $\ddot{\text{Cl}}$:, H : $\ddot{\text{O}}$: H, : $\ddot{\text{O}}$: : C : : $\ddot{\text{O}}$: are diamagnetic, but nitric oxide : $\dot{\text{N}}$: : $\ddot{\text{O}}$: (or : $\ddot{\text{N}}$: : $\dot{\text{O}}$:), oxygen : $\dot{\text{O}}$: $\dot{\text{O}}$: (see p. 270), nitrogen dioxide : $\ddot{\text{O}}$: : $\dot{\text{N}}$: : $\ddot{\text{O}}$: and chlorine dioxide : $\ddot{\text{O}}$: : $\dot{\text{Cl}}$: : $\ddot{\text{O}}$: are paramagnetic. These are all "odd molecules," except oxygen, which has *two* uncoupled electrons and might be called "doubly odd." Its magnetic moment is about double that of nitric oxide.

Hypophosphoric acid was formerly represented by the formula H_2PO_3, but this molecule would contain an odd number of electrons ($2 + 15 + 18 = 35$) and the salts should be paramagnetic. As they are diamagnetic, the formula must be doubled to $H_4P_2O_6$ and this agrees with the determined molecular weight of the ester, $(C_2H_5)_4P_2O_6$ (p. 616).

The yellow solid potassium nitrosodisulphonate $(KSO_3)_2NO$ (p. 588) is diamagnetic and is therefore probably dimeric $[(KSO_3)_2NO]_2$, but the solution is deep blue and paramagnetic (Asmussen, 1933), hence it probably contains

O
::
$KSO_3 : \dot{N} : SO_3K$.

Miscellaneous methods.—In the molecules of N_2O and CO_2 as formulated by Langmuir (see Fig. 113) :

$\ddot{\text{N}} : : \text{N} : : \ddot{\text{O}}$ and $\ddot{\text{O}} : : \text{C} : : \ddot{\text{O}}$,

each atom has the same external configuration as neon, a nucleus surrounded by an inner shell of two, and an outer shell of eight, electrons. By measurement of the viscosities of the gases, the area offered to collision by the molecules may be calculated, and it is concluded that the CO_2 and N_2O molecules behave not only

as if they had the same size and shape, but also as if each had practically the same outer electron configuration as three neon atoms placed together in line.

Information on the outer electron configuration of atoms and molecules is given by the **Ramsauer effect**—the stopping power of the particle for slow-moving electrons. In this way $H_2(1+1)$ and He, with 2 outer electrons; Ne, A, Kr, Xe, $CH_4(4+4)$ and $HCl(1+7)$, with 8 outer electrons, behave similarly. In the band spectra also, the effects due to the electrons are alike with H_2 and He; with Na, BeF, BO, CN, CO^+ and N_2^+ (all with 8 outer electrons); and with Mg, CO and N_2 $(8+2$ outer electrons).

Hydrogen compounds.—By analogy with the Russell-Soddy displacement law (p. 203), Grimm (*Z. Elektrochem.*, 1924, **30**, 467) suggested that, as the addition of a proton H^+ to the atomic kernel should lead to the same result as the expulsion of an electron, *e.g.* hypothetically $O^{--}+H^+=F^-$ (from At. No. 8 of oxygen we arrive at At. No. 9, an isotope of fluorine), so the actual process $O^{--}+H^+=OH^-$ should lead to a compound OH^- similar to the fluorine ion. In this way elements occupying the four places before an inert gas, by taking up 1, 2, 3 and 4 hydrogen atoms, form " pseudo-atoms " which resemble the atoms of elements in the groups 1, 2, 3 or 4 places to the right. This is illustrated by the following table, in which the compounds, ions or radicals in the same vertical column show similar properties:

	Group → IV	V	VI	VII	O	I
H-atoms 0	C	N	O	F	Ne	Na
1	CH	NH	OH	FH		
2		CH_2	NH_2	OH_2	FH_2?	
3			CH_3	NH_3	OH_3	
4				CH_4	NH_4	
Valency	−4	−3	−2	−1	0	+1

Radius ↓ ← Radius

Covalent compounds and salts.—The values of the electrical conductivity at the melting point of the chlorides of groups of elements in the periodic system show that they fall into two classes divided by the line shown below:

HCl					
LiCl	$BeCl_2$	BCl_3	CCl_4		
NaCl	$MgCl_2$	$AlCl_3$	$SiCl_4$	PCl_5	
KCl	$CaCl_2$	$ScCl_3$	$TiCl_4$	VCl_4	
RbCl	$SrCl_2$	YCl_3	$ZrCl_4$	$NbCl_5$	$MoCl_5$
CsCl	$BaCl_2$	$LaCl_3$	$HfCl_4$	$TaCl_5$	WCl_6
			$ThCl_4$		UCl_4

Those above the line are non-conductors or very poor conductors, and hence are covalent compounds, whilst those below the line are good conductors and are electrovalent salts.

The first element or few elements of a group form covalent linkages and the others exhibit electrovalencies. (In water, $BeCl_2$ forms a conducting ionic solution.)

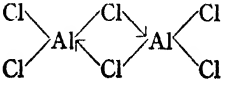
Hydrogen chloride is covalent, but ionises in a suitable solvent. This is due to the attraction of the proton (H^+) by the solvent molecule to form a solvated hydrion : $HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$. The tendency of the negative radical part of the molecule to attract an electron and form an anion also plays a part in promoting ionisation ; whereas HCl is strongly ionised both in water and alcohol, forming $(H_2O{\cdot}H)^+$ and $(C_2H_6O{\cdot}H)^+$, nitric acid is only slightly ionised in alcohol, presumably because the NO_3 radical has only a small electron-attracting power.

Covalent solids usually have low *melting points* unless they have high molecular weights, whilst ionic salts usually have high melting points. Some covalent solids such as diamond have high melting points, but are atomic lattices or " macromolecules " (p. 246). The melting point is, however, a doubtful criterion of covalency.

Covalent solids often have greater *volatility* than salts, but again there are exceptions, and although the greater volatility of SiF_4 as compared with AlF_3, for example, has been explained by assuming that SiF_4 has covalent links while AlF_3 is a salt with ionic links, it is probable that the bonds are very similar and that the effect is due to the atomic arrangement in the solids.

In AlF_3 each aluminium is surrounded by six fluorines and the crystal is a giant polymer with the atoms linked by strong chemical bonds. In SiF_4 each silicon is surrounded by four fluorines and the individual SiF_4 molecules are held together by weak van der Waals forces (Kossel, *Z. Phys.*, 1920, **1**, 395 ; Pauling, *J.A.C.S.*, 1932, **54**, 988, 3570).

In the case of aluminium chloride the molecules are associated by coordinate links (Palmer and Elliott, *J.A.C.S.*, 1938, **60**, 1852) :



PART II

INORGANIC CHEMISTRY

CHAPTER XI

HYDROGEN

AN inflammable gas (*gas pingue*) is mentioned by van Helmont (d. 1644) and was collected from iron and an acid by Turquet de Mayerne (d. 1655) and Boyle (1672). It was carefully studied by Cavendish in 1766, who called it *inflammable air*. The name hydrogen (from the Greek *hudor*, water) is due to Lavoisier.

Traces (0·00001 p.c.) of free hydrogen are said to occur in the atmosphere; it is found in volcanic gases (up to 30 p.c. by vol.) and in small cavities in rock-salt, and is evolved on heating many minerals and rocks. Iron meteorites contain occluded hydrogen, and the spectroscope shows that the outer atmosphere of the sun consists largely of this gas; it is the chief constituent of the solar prominences, which are parts of the chromosphere seen as huge red flames of incandescent gas in total eclipses. It is also detected in nebulae and in most stars.

Free hydrogen is evolved in certain types of anaerobic fermentation of carbohydrates brought about by specific bacteria, *e.g.* along with carbon dioxide in the fermentation of starch in the industrial preparation of butyl alcohol and acetone.

Many compounds of hydrogen occur naturally. The commonest is water H_2O; the halogen acids HF, HCl, HBr and HI, and hydrogen sulphide H_2S, are found in volcanic gases. Traces of ammonia NH_3 occur in the atmosphere. All organic substances contain hydrogen.

There are three *isotopes of hydrogen*, with the approximate atomic masses 1, 2 and 3: the common form is ^1H (sometimes called *protium*); ^2H or D, *deuterium*, occurs in natural hydrogen in the approximate and nearly constant ratio $^1H : D = 6900 : 1$ (Swartout and Dole, *J.A.C.S.*, 1939, **61**, 2025), mostly as HD (which might be called *mesium*); ^3H or T, *tritium*, is formed in the artificial disintegration of deuterium (p. 207): $^2D + {}^2D = {}^3T + {}^1H$, but does not occur naturally in appreciable amount.

Preparation of hydrogen.—Hydrogen may be prepared from *water* by electrolysis or the action of some metals or of carbon; from *acids* and *alkalis* by the action of metals; and by some special processes.

In the **electrolysis** of acidulated water in a voltameter 2 vols. of hydrogen are evolved at the cathode and 1 vol. of oxygen at the anode.

Bunsen's voltameter has for anode a pool of zinc amalgam in dilute sulphuric acid: this absorbs the oxygen deposited and pure hydrogen is evolved from the platinum cathode.

Very *pure hydrogen* is evolved at the cathode in the electrolysis, with nickel electrodes, of a warm concentrated solution of barium hydroxide in a hard glass U-tube (H. B. Baker, *J.C.S.*, 1902, **84**, 400). The gas is passed over heated platinum gauze (not platinised asbestos, which forms some silicon hydride) to burn out any oxygen, and is dried by passing over broken pieces of potassium hydroxide, followed by purified phosphorus pentoxide (which has been sublimed in oxygen). A little nitrogen (from air leaks) is removed by passing the hydrogen into a heated exhausted glass bulb containing pieces of palladium foil, and the metal is allowed to cool in the gas. The palladium takes up a large volume of hydrogen and the residual nitrogen is pumped out of the bulb. On heating the bulb, the pure hydrogen is evolved from the palladium (Fig. 165).

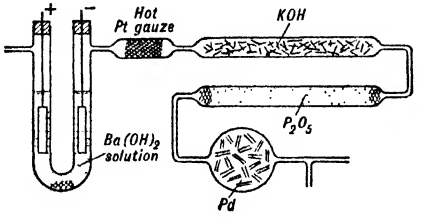


FIG. 165.—Preparation of pure hydrogen.

On the large scale electrolytic hydrogen is made from dilute sodium or potassium hydroxide electrolysed in a divided cell with iron or nickel electrodes. It may be formed directly under pressure when compressed hydrogen is required. Large quantities of by-product hydrogen are evolved in the electrolytic production of chlorine and sodium hydroxide (p. 773).

Hydrogen is set free by the action of many *metals on water* under various conditions. The action is more vigorous the more electropositive (p. 97) the metal, as it is essentially $M + xH^+ = M^{x+} + \frac{1}{2}xH_2$. *Cold water* is rapidly decomposed by the alkali metals (Li, Na, K, Rb and Cs), the violence of the reaction increasing in order from lithium to caesium, so that the liberated hydrogen is inflamed with K, Rb and Cs: $2M + 2H_2O = 2MOH + H_2$. Cold water is slowly decomposed by the alkaline earth metals Ca, Sr and Ba, and by magnesium powder: $M + 2H_2O = M(OH)_2 + H_2$. *Hot water* is rapidly decomposed by magnesium powder and by copper-zinc couple (made by depositing copper on zinc foil or granulated zinc from copper sulphate solution), and slowly by reduced iron. Some heated metals decompose *steam*: magnesium continues to burn in steam; red-hot zinc, iron, manganese, chromium, cobalt, and possibly nickel, decompose steam, forming oxides; strongly heated tin, lead, antimony and bismuth, and (at very high temperatures only) copper, decompose steam, forming oxides.

Sodium amalgam, amalgamated aluminium and an alloy of sodium and lead decompose cold water slowly. With very pure sodium amalgam and water the action is slow, bubbles appearing at isolated points on the amalgam; adding ordinary distilled water accelerates the action, apparently owing to the presence of a trace of hydrogen peroxide (H. B. Baker and L. H. Parker, *J.C.S.*, 1913, **103**, 2060). Calcium hydride (*hydrolith*) has been used commercially in preparing hydrogen:

$$CaH_2 + 2H_2O = Ca(OH)_2 + 2H_2.$$

Hydrogen is freely evolved when a current of steam is passed over iron borings or small nails in a silica or iron tube heated to redness. The action is incomplete and water may be condensed in a cooled flask, the hydrogen passing on (Lavoisier, 1784):

$$3Fe + 4H_2O \rightleftharpoons Fe_3O_4 + 4H_2.$$

The reaction is reversible and exothermic, the amount of hydrogen decreasing with rise of temperature:

Temperature - - -	200°	444°	860°	918°
Ratio H_2/H_2O by volume	20·9	5·6	2·78	2·00

In the *Lane process* reduced iron (from spathic iron ore) is heated at 600°–850° in vertical iron retorts and steam passed over it. The iron oxide is reduced again by the hydrogen and carbon monoxide of water gas (see below), and the steaming and reduction processes alternate. The gas contains 98 p.c. of hydrogen and a little carbon monoxide.

Water gas, a mixture of hydrogen, carbon monoxide and carbon dioxide, is made by passing steam over red-hot carbon, the amount of carbon monoxide increasing with the temperature:

$$C + 2H_2O = CO_2 + 2H_2 \text{ (dull red heat)},$$
$$C + H_2O = CO + H_2 \text{ (bright red heat)}.$$

In the *Bosch process* a mixture of water gas and steam is passed over a catalyst of ferric oxide and promoters such as chromium oxide (Cr_2O_3) at 450°–500°. The carbon monoxide is oxidised by the steam: $CO + H_2O \rightleftharpoons CO_2 + H_2$, the carbon dioxide formed is removed by washing the gas at 25 atm. pressure with water, and the trace of carbon monoxide remaining is removed by washing the gas at 200 atm. pressure with ammoniacal cuprous formate solution. The hydrogen, when dried, is at least 99·9 p.c. pure.

Carbon monoxide can also be removed from water gas by strong cooling, when it liquefies (b.p. −191·5°) leaving the hydrogen (b.p. −253°) gaseous. Hydrogen is made in California by the thermal decomposition of natural gas (methane, $CH_4 = C + 2H_2$) or gases from petroleum "cracking", or else the natural gas is mixed with steam and heated: $CH_4 + 2H_2O = CO_2 + 4H_2$.

Hydrogen is evolved by the action of certain *acids on metals*:

$$M + 2H^{\cdot} = M^{\cdot\cdot} + H_2.$$

It is prepared in the laboratory by the action of dilute hydrochloric acid (1 vol. conc. acid to 4 vols. water) or sulphuric acid (1 vol. acid to 5 vols. water) on granulated or stick zinc:

$$Zn + 2HCl = ZnCl_2 + H_2$$
$$Zn + H_2SO_4 = ZnSO_4 + H_2.$$

These dilute acids also evolve hydrogen with magnesium and iron, and concentrated hydrochloric acid with aluminium and tin (on heating). Nitric acid does not evolve hydrogen, but oxides of nitrogen, with metals, except with cold dilute (1–2 p.c.) acid and magnesium or manganese. A solution of mercuric chloride acidified with hydrochloric acid evolves hydrogen from aluminium.

Before collecting the gas over water or by upward displacement a little collected in a test-tube should *burn* quietly and not explode (as happens when the air has not been displaced from the apparatus). The gas from zinc and dilute sulphuric acid may contain some hydrogen sulphide, especially if the acid is hot or the zinc not quite pure (see p. 714). The gas from commercial zinc and acid may be *purified* by passing over red-hot copper turnings, or through a saturated solution of potassium permanganate, followed by a 5–10 p.c. solution of silver nitrate; hydrogen sulphide, phosphide and arsenide, and oxides of nitrogen, sulphur dioxide, and volatile hydrocarbons, are removed. Unless hot copper is used a little oxygen remains, but may be removed by a solution of chromous chloride.

Hydrogen is *dried* by passing over granular calcium chloride or broken sticks of caustic potash, and completely by purified phosphorus pentoxide. Concentrated sulphuric acid is liable to form some sulphur dioxide:

$$H_2SO_4 + H_2 = SO_2 + 2H_2O,$$

unless cooled in a freezing mixture, and is not recommended for drying hydrogen (cf. Milbauer, *Z. phys. Chem.*, 1907, **57**, 649).

Hydrogen is sometimes evolved by the action of *alkalis on metals*. A warm 20–30 p.c. solution of sodium or potassium hydroxide dissolves zinc or silicon, and warm dilute alkali dissolves aluminium, with evolution of hydrogen and formation of a zincate, silicate or aluminate (containing the metal or silicon in the anion):

$$Zn + 2KOH = K_2ZnO_2 + H_2$$
$$2Si + 2NaOH + 3H_2O = Na_2Si_2O_5 + 4H_2$$
$$2Al + 2NaOH + 2H_2O = 2NaAlO_2 + 3H_2.$$

In the technical *silicol process* a 25 p.c. solution of caustic soda and powdered silicon (or silicon-iron alloy containing at least 80 p.c. of silicon) are used. *Hydrogenite* is a mixture of 25 parts of silicon, 60 of caustic soda and 20 of slaked lime. When kindled it burns, evolving 270–370 lit. of H_2 per kg. and leaves sodium and calcium silicates. (On technical hydrogen see P. L. Teed, *The Chemistry and Manufacture of Hydrogen*, 1919; H. C. Greenwood, *Industrial Gases*, 1920.)

Properties of hydrogen.—Pure hydrogen is a colourless, odourless and tasteless gas which does not support respiration, but is not poisonous unless it contains impurities (CO, AsH_3, etc.). When breathed with some air for a short time it weakens the voice and raises its pitch. It is the lightest gas:

Normal density 0·08987 g./lit. b.p. −252·78° m.p. −259°
Critical temperature −239·9° Critical pressure 12·8 atm.
Density of liquid at −258° and 745·52 mm. pressure 0·07105.

Air is 14·4 times denser than hydrogen, or if air = 1 the relative density of hydrogen is 0·069. Hydrogen is used in filling balloons and the gas-containers of airships. It is sparingly soluble in water, the Bunsen's absorption coefficient (p. 55) not varying much with temperature:

0° 0·0215 10° 0·0198 15° 0·0190 20° 0·0184 100° 0·0160.

The solubility in alcohol is four, and in petroleum three times, that in water.

The spectrum of hydrogen, obtained with an electrical discharge in the gas at low pressure, shows four bright lines of the Balmer spectrum, due to atomic hydrogen, and used in calibrating spectroscopes or refractometers: red H_α 6563 A., greenish-blue H_β 4861 A., blue H_γ 4340 A., and indigo H_δ 4102 A.

Hydrogen is the best conductor of heat of all gases, about five times as good as air, and its specific heat, $c_p = 3{\cdot}4$ g. cal. per g. at 0°, is also abnormally high. If a spiral of platinum wire, heated to redness by an electric current, is inserted into an inverted jar of hydrogen, the wire ceases to glow on account of the increased loss of heat to the gas (Andrews, 1840). At high temperatures dissociation into atoms occurs (p. 286): $H_2 \rightleftharpoons 2H$, the reaction absorbing a large amount of heat (about 100 k. cal. per mol.).

Hydrogen, with a low critical temperature, is difficult to liquefy (p. 40). *Liquid hydrogen* is colourless and transparent, with the very small density of 0·071 at the m.p.; by rapid evaporation under reduced pressure in a Dewar tube immersed in liquid hydrogen in an outer Dewar vessel it freezes to colourless transparent (or snow-like) *solid hydrogen*.

Hydrogen is combustible, burning in air or oxygen with a very pale blue flame to form water: $2H_2 + O_2 = 2H_2O$. If a wide glass tube is brought over a jet of burning hydrogen a musical note is produced. A mixture of hydrogen with air or oxygen explodes violently when kindled.

Hydrogen and oxygen combine slowly at 180° or in bright sunlight at the ordinary temperature. Explosion occurs at 550°–700° with moist gases, but very pure and dry gases combine with great reluctance and without explosion when heated, *e.g.* by an incandescent silver wire (H. B. Baker, *J.C.S.*, 1902, **84**, 400; Bone and Andrew, *J.C.S.*, 1906, **89**, 652; Dixon, *J.C.S.*, 1910, **97**, 661; Coehn and Tramm, *Ber.*, 1923, **56**, 455). When slow combination occurs with less dry gases the water formed is so pure that it has no catalytic influence on the reaction. Coehn and Tramm (1923) say intensive drying does not affect the rate of combination in ultra-violet light, but Baker and Carlton (*J.C.S.*, 1925, **127**, 1990) say it retards it.

The mixture $2H_2 + O_2$ ignites at 526° on adiabatic compression, some combination occurring before the explosion itself (pre-flame period); $3H_2 + O_2$ ignites at 544°, and $H_2 + 4O_2$ at 478° (Dixon and Crofts, *J.C.S.*, 1914, **105**, 2036). Thomas Thomson in 1817 gave 538° as the ignition temperature of hydrogen in air.

Hydrogen readily combines with fluorine and chlorine, less readily with bromine, iodine, sulphur, phosphorus, nitrogen, and carbon. With a few metals, such as lithium, sodium, and calcium, it forms **hydrides**, such as NaH, on heating. These when pure are white salt-like compounds (KH explodes in air), readily decomposed by water:

$$NaH + H_2O = NaOH + H_2.$$

In alkali metal hydrides the hydrogen behaves like a halogen or electronegative element. On electrolysis of fused lithium hydride, the hydrogen is liberated at the *positive* electrode (Moers, 1920; Peters, 1923). Hydrogen is evolved at the anode in the electrolysis of a solution of calcium hydride CaH_2 in fused potassium and lithium chlorides (Bardwell, *J.A.C.S.*, 1922, **44**, 2499).

On account of its affinity for oxygen, hydrogen acts as a *reducing agent.* When passed over many heated metallic oxides it reduces them to the metals, and water is produced.

The oxy-hydrogen and oxy-acetylene blowpipes.—When oxygen and hydrogen are supplied separately to a blowpipe jet (Fig. 166) a blue, pointed, intensely

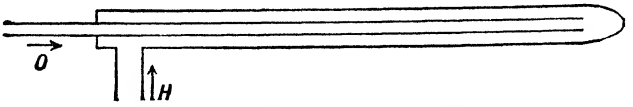


FIG. 166.—Oxy-hydrogen blowpipe.

hot (*c.* 2800°) flame is produced. Platinum wire readily melts in this flame. Carbon monoxide gives a flame temperature of about 2600°. If the **oxy-hydrogen** (or oxy-coal gas) **flame** impinges on a small cylinder of quicklime, an intensely white light is emitted by the incandescent infusible lime, formerly used as *limelight* (Drummond, 1826). The oxy-hydrogen blowpipe is used in fusing quartz and platinum and in making fused silica apparatus, *e.g.* mercury lamps. An air-hydrogen blowpipe is used in the autogenous welding of lead, pure lead being melted over the joint.

In the *oxy-acetylene blowpipe* a still hotter flame (3100°–3315°) is obtained. The steam formed is almost completely dissociated :

$$C_2H_2 + O_2 = 2CO + H_2.$$

The flame is strongly reducing and suitable for welding metals. In cutting iron or steel a third inner tube is used, and when the metal is heated to a high temperature this inner oxygen jet is turned on. The iron burns brilliantly, emitting showers of sparks, and rapidly fuses away. The oxygen jet is narrow and a very clean cut is produced. Plates of steel 12 in. thick can be rapidly cut through in this way. Coal gas may also be used.

The acetylene and oxygen are used in the proportions 1·5 vols. of O_2 : 1 vol. of C_2H_2, the acetylene being generated from calcium carbide and water or more conveniently used dissolved under pressure in acetone, soaked in a porous material contained in steel cylinders. (Compressed acetylene *gas* is liable to explode spontaneously.) The porous material may be " kapok," the seed-hairs in the pods of a tree (*Eriodendron anfractuosum*) growing in India and Java.

Atomic hydrogen.—Langmuir (*J.A.C.S.*, 1912–16) found that hydrogen at low pressure in contact with a tungsten wire strongly heated by an electric current is dissociated into atoms : $H_2 \rightleftharpoons 2H$. This absorbs a large amount of energy, 102·8 k. cal. per mol, and atomic hydrogen is chemically very active. The volume percentages of dissociation at different pressures are :

$T°$ abs. -	2000	2500	3500	4000
760 mm. -	0·33	3·1	34	61
1 mm. -	8·7	57·5	99·3	99·9

It forms hydrides at room temperature with sulphur, phosphorus, arsenic and many metals, combines with chlorine in the dark, and forms hydrogen

peroxide with molecular oxygen: $2H + O_2 = HO{\cdot}OH$. It reduces many oxides and salts in the cold and adds to unsaturated hydrocarbons. It does not combine with molecular nitrogen, but gives formaldehyde with carbon monoxide: $2H + CO = H{\cdot}CO{\cdot}H$.

Langmuir showed that atomic hydrogen is formed in an electric arc between tungsten electrodes in hydrogen gas at atmospheric pressure (Fig. 167).

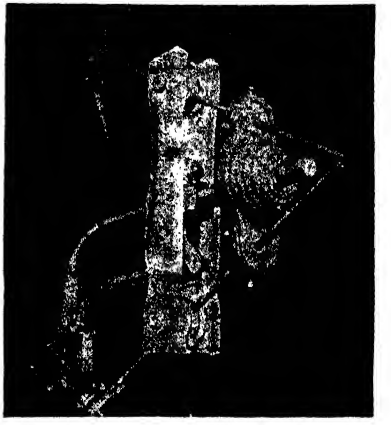


FIG. 167.—The atomic hydrogen blowpipe.

Hydrogen gas issues from the central nozzle on the right and is dissociated in an electric arc between two tungsten rods nearly meeting in a V.

The atomic hydrogen blown out by a jet of molecular hydrogen directed across the arc forms an intensely hot flame capable of melting tungsten (m.p. 3400°). This obtains its heat not from combustion, but from the recombination of hydrogen atoms to H_2. It is suitable for melting and welding many metals. Iron can be melted without contamination with carbon, oxygen, or nitrogen. Because of the powerful reducing action of the atomic hydrogen, alloys can be melted without fluxes and without surface oxidation. A feature of the flame which is important in welding is the great rapidity with which heat can be delivered to a surface which catalyses the reaction $2H = H_2$.

Atomic hydrogen is also formed by the action of an electric discharge on a stream of hydrogen at low pressure (R. W. Wood, 1920). Some gaseous H_3^+ ions are also formed, but the neutral H_3 molecule is unknown, the reactions once reported for it being due to impurities such as silicon hydride, which is formed when hydrogen is passed over heated platinised asbestos (Paneth, etc., 1927; Hiedemann, 1931).

Nascent hydrogen.—Hydrogen set free in a chemical reaction is often more reactive than hydrogen gas, and is called *nascent hydrogen*. Laurent (1846) suggested that it is *atomic hydrogen* existing for a short time before combination to hydrogen molecules occurs.

Ferric salts are reduced to ferrous salts by zinc and dilute sulphuric or hydrochloric acid: $FeCl_3 + H = FeCl_2 + HCl$. No change is produced by bubbling gaseous hydrogen through the solution. Zinc and dilute sulphuric acid reduce potassium chlorate to potassium chloride.

The atomic theory of nascent hydrogen is confirmed by the formation of hydrogen peroxide when oxygen is bubbled round a cathode at which hydrogen is liberated electrolytically (Taylor, 1926), since Langmuir showed that this reaction occurs with gaseous hydrogen atoms: $2H + O_2 = HO{\cdot}OH$. Another theory is that the hydrogen is given off in very small bubbles under *great pressure*; hydrogen gas under pressure reduces some metallic salts (*e.g.* $AgNO_3$) in solution (Beketoff, 1859). It appears that the chemical action producing the

hydrogen is important (Tommasi, 1879), because potassium chlorate is not reduced by sodium amalgam, which reduces nitrites to hyponitrites. Zinc reduces nitrites to ammonia in presence of alkali. Zinc amalgam is often more active than zinc, especially if a trace of copper salt is added, and " couples " of zinc with copper or iron are used for reduction. Hydrogen for reducing purposes may be liberated in alkaline solution by zinc or aluminium, and in neutral (aqueous) solution by copper-zinc couple or amalgamated aluminium. Gaseous hydrogen in presence of platinum or palladium black, and especially colloidal palladium, is a good reducing agent for solutions. Nascent hydrogen liberated at the cathode in electrolysis is also used for reduction. At higher temperatures, hydrogen gas in presence of finely divided nickel is used to produce solid fats from liquid oils in making margarine.

Ortho- and para-hydrogen.—The hydrogen molecule consists of two protons and two electrons. The *protons* can have their spins in the same or in opposite senses, and two different kinds of hydrogen molecule result, known as *ortho*-hydrogen and *para*-hydrogen, respectively.

Dennison (1927) showed that the specific heat curves of hydrogen at low temperatures could be explained if ordinary hydrogen is a mixture of these two kinds of molecules in the ratio of 3 to 1. Evidence of these in liquid hydrogen was found by an optical method by McLennan and McLeod early in 1929.

In 1929 Bonhoeffer and Harteck found that when ordinary hydrogen is cooled and compressed, conversion of ortho- into para-hydrogen occurs. On adsorbing ordinary hydrogen on charcoal at the temperature of liquid hydrogen there is practically complete catalytic conversion into parahydrogen, which may be pumped off as gas.

There is no known way of obtaining pure orthohydrogen. Ordinary hydrogen is the richest mixture, 3 parts of ortho- and 1 part of para-hydrogen. Parahydrogen has a slightly lower freezing point and boiling point, and is a much better conductor of heat, than orthohydrogen, or ordinary hydrogen (a fact used in finding the proportions of the two in a mixture). The specific heat-temperature curves of the two forms are quite different, parahydrogen having a maximum rotational specific heat (p. 34) at 170° abs.

When atomic hydrogen is mixed with parahydrogen (opposite proton spins) it pairs with one of the atoms in the molecule, forming orthohydrogen (parallel proton spins) and liberating a hydrogen atom :

$$H + H_2 = H_2 + H$$

$$\boxed{\uparrow \quad \uparrow}\downarrow \qquad \uparrow\uparrow \qquad \downarrow$$

This reaction is used in detecting atomic hydrogen in a gas, *e.g.* that formed in the photochemical combination of hydrogen and chlorine (p. 784).

The occlusion of hydrogen by metals.—Deville and Troost (1863) found that platinum and iron are permeable to hydrogen at a red heat, and concluded that " metals and alloys have a certain porosity." Graham (1866–69 ; *Researches*, 1876, p. 253) showed that the penetration cannot be due to porosity, since hydrogen is practically the only gas which shows the effect. Helium (with

smaller molecules) will not pass through platinum or palladium, although it readily penetrates hot glass or silica.

Graham heated in air a platinum bulb filled with hydrogen. In half an hour 97 p.c. of the hydrogen passed out but no air entered. Five hundred c.c. of hydrogen passed per sq. m. per minute through a platinum tube 1·1 mm. thick. Through a similar palladium tube the hydrogen began to escape at 100°, and at a red heat 3993·2 c.c. passed out per sq. m. per minute. No other gas except ether vapour penetrated the metal. Palladium in a glass tube was exposed to hydrogen at 90°–97° for three hours and allowed to cool in the gas for ninety minutes. When the tube was heated by a flame and the gas pumped off, the metal yielded 643 times its volume of gas. Upwards of 500 vols. of gas were given out at 245° in a vacuum.

Graham did not think a chemical compound was formed; in 1868 he said: "the whole phenomenon appears to be consistent with the solution of liquid hydrogen in the metal.... It may be allowed to speak of this as the power to occlude (to shut up) hydrogen, and the result as the occlusion of hydrogen by platinum." In 1869 he suggested that hydrogen was the vapour of a volatile metal *hydrogenium*, which forms an alloy with palladium, but when solid hydrogen was later obtained it was found to be a transparent solid, with no metallic properties. It is probable, however, that the hydrogen in palladium is in the *atomic* form.

The hydrogen occluded in palladium is a strong *reducing agent*: it precipitates mercury from mercuric chloride solution, combines with chlorine and iodine in the dark, and reduces ferric to ferrous salts. Colloidal palladium takes up 2950 vols. of hydrogen and is a very strong reducing agent.

EXPT. 1.—The occlusion of hydrogen by palladium is shown by using two strips of palladium foil in dilute sulphuric acid as electrodes. Oxygen is evolved from the anode but no gas is evolved from the cathode until the metal becomes charged with hydrogen, when bubbles come off. If the current is reversed no gas comes from either electrode for a time; the oxygen is combining with the occluded hydrogen in one electrode and hydrogen is being occluded in the other. After a time gas comes from both electrodes. The palladium strips bend, owing to the unequal expansion on absorption of hydrogen. Sometimes gas is slowly evolved from the metal after the current is switched off, owing to supersaturation.

Troost and Hautefeuille (*Compt. rend.*, 1874, **78**, 686) pumped off hydrogen occluded in palladium in a glass tube and measured the pressures at a given temperature. The first portions of gas came off readily, but when 600 vols. of hydrogen were left to 1 vol. of palladium, the rest of the gas came off at constant pressure, as does water vapour from a salt containing water of crystallisation. Hence these observers concluded that a definite *hydride of palladium* was present, together with palladium. The Phase Rule (p. 51) shows that *two solid phases* are present: $C=2$ and $F=1$, $\therefore P=C+2-F=3$ (1 gas and 2 solids). Constant pressure intervals were observed at different temperatures.

The density of palladium is 12, hence the ratio of the weights of palladium and hydrogen in the metal which has occluded 633 vols. of hydrogen is $12 : 633 \times 0{\cdot}00009 = 12 : 0{\cdot}057$, hence the ratio of the atoms in palladium saturated with hydrogen is $Pd : H = 2{\cdot}0 : 1$, corresponding with Pd_2H.

Roozeboom and Hoitsema (*Z. phys. Chem.*, 1895, **17**, 1) found that the pressure curves at temperatures between 0° and 190° consist of *three* parts (Fig. 168), two rapidly ascending parts joined by a nearly horizontal but slowly rising middle portion. At higher temperatures the flat part became shorter. It was less flat if palladium black was used instead of foil. The dotted curves give the results of Troost and Hautefeuille. The shapes of the curves were considered by Roozeboom and Hoitsema to speak against the existence of a definite compound; with certain reservations they concluded that the flat part of the curve where the pressure is practically constant, indicates that *two solid solutions* are present. They pointed out that the hydrogen used contained a little nitrogen, which would explain the upward slope of the curves, and did not consider the experiments sufficient to decide the question, although they have been widely quoted as evidence against compound formation.

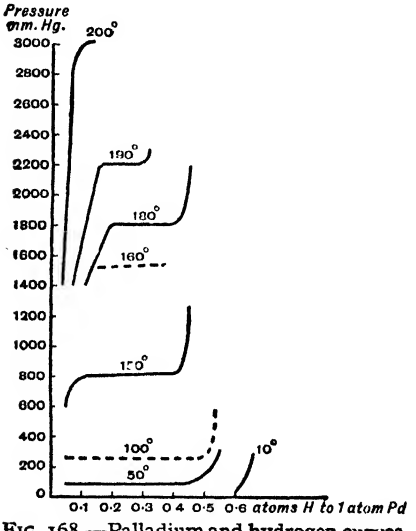


FIG. 168.—Palladium and hydrogen curves.

Holt, Edgar, and Firth (*Z. phys. Chem.*, 1913, **82**, 513; **83**, 507) concluded that the hydrogen exists partly as a condensed layer on the surface and partly dissolved in the interior of the metal, and is not usually homogeneously distributed.

They found that palladium is normally inactive but becomes active by (*a*) oxidation by heating in air and reduction in hydrogen, (*b*) heating to 400°, and then cooling, in hydrogen, (*c*) heating to 400° *in vacuo*—hydrogen must then be admitted as soon as cold, as the metal soon loses its activity. The rate of diffusion of hydrogen through palladium 0·3 mm. thick was 3288 c.c. per sq. m. per minute at 200°, and 5570 c.c. at 476°.

By pumping out a palladium tube saturated with and surrounded with hydrogen, the pressure inside was reduced to zero at the ordinary temperature, whilst the pressure on the other side was 10·4 mm. At 140°, with two pumps working equally on both sides, the outer surface lost 208 c.c. of gas and the inside only 12 c.c. The surface layer is easily removed but the gas in the interior of the metal is more firmly held.

Gillespie and Hall (*J.A.C.S.*, 1926, **48**, 1207) obtained states of true equilibrium by using finely divided palladium and special heat treatment. They obtained horizontal isotherms (Fig. 169) and found evidence of two immiscible solid solutions, but at temperatures of 80°, 160° and 180° the one richer in hydrogen had practically the composition Pd_2H, which they regard as a definite compound separating nearly pure except at lower temperatures, when it dissolves increasing amounts of hydrogen.

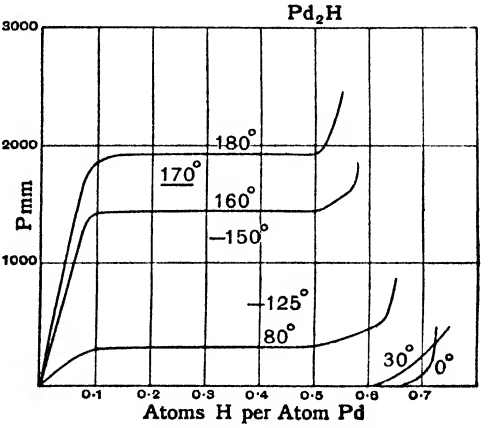


FIG. 169.—Gillespie and Hall's results.

Gillespie and Galstaun (*J.A.C.S.*, 1936, **58**, 2565) repeated the experiments over a wider range of temperature and concluded that there are vertical steps of the boundary curves on both sides of the flat portions, which steps correspond with Pd_8H and Pd_4H on the hydrogen-poor side of the diagram, and Pd_3H and Pd_2H on the hydrogen-rich side, at lower and higher temperatures, respectively. No evidence of PdH was found. At 295° the two solid phases become miscible at a kind of critical point. Gillespie and Downs (*J.A.C.S.*, 1939, **61**, 2496) investigated the palladium-deuterium system.

DEUTERIUM

As a result of a supposed discrepancy between the chemical and mass spectrograph atomic weights of hydrogen, Birge and Menzel in 1931 suggested that ordinary hydrogen contains a small amount of a heavier isotope of mass 2, and this was recognised spectroscopically in 1931 by Urey, Brickwedde and Murphy, who called it *deuterium*, D. The partial separation of " heavy water " or deuterium oxide D_2O from ordinary water by prolonged electrolysis was effected in 1932 by Washburn and Urey, and in 1933 G. N. Lewis and Macdonald prepared nearly pure deuterium oxide and investigated its properties. Ordinary hydrogen contains about 1 part of deuterium to 6900 of " light hydrogen " (*protium*), and ordinary water contains a corresponding amount of D_2O. The ratio H : D varies very slightly in waters from different sources (Briscoe, etc., *J.C.S.*, 1934, 1207, 1948; Dole, etc., *J.A.C.S.*, 1939, **61**, 2025), the D_2O content being measured by small differences in density.

The principal method of enrichment of water in deuterium oxide is electrolysis; the light hydrogen is preferentially evolved, probably owing to the different overvoltages (p. 122) of the two hydrogens, and by prolonged electrolysis (the later fractions of evolved hydrogen, rich in deuterium, being burnt and returned to the cell) pure D_2O can finally be obtained. It is made commercially by the Norsk Hydro. Co., and then contains about 0·38 p.c. of $D_2{}^{18}O$

(containing heavy oxygen) (Tronstadt, etc., *T. Faraday Soc.*, 1938, **34**, 766). Other methods of separation are of little practical interest, although fractional distillation is not without promise.

From deuterium oxide, gaseous deuterium D_2 is obtained by dropping the liquid on sodium: $2D_2O + 2Na = 2NaOD + D_2$, or (with less loss) by electrolysis of deuterium oxide in which phosphorus pentoxide has been dissolved.

The physical properties of "normal" hydrogen and deuterium, and of "normal" water and deuterium oxide, are given below.

	H_2	D_2	H_2O	D_2O
Density D_{25}^{25}	—	—	1·00000	1·10764
Temperature of maximum density	—	—	4·0° C.	11·23° C.
Boiling pt.	20·38° Abs.	23·50° Abs.	100° C.	101·42° C.
Freezing pt.	13·95° Abs.	18·65° Abs.	0° C.	3·802° C.
Triple pt.	13·92° Abs.	18·58° Abs.	0·0077° C.	3·809° C.
Specific heat (20°)	—	—	1·000	1·018
Critical temperature	—	—	374·2° C.	371·5° C.
Latent ht. of evap. (g. cal./mol)	219·7	302·2	9700	9960
Latent ht. of fusion (g. cal./mol)	28	47	1436	1510
Molar vol. of solid (ml).	23·31	20·48	19·66	19·68
Viscosity at 20° (millipoises)	—	—	10·09	12·60
Surface tension at 20° (dynes/cm.)	—	—	72·7	72·8
Refractive index n_D^{20}	—	—	1·33300	1·32844
Magnetic mass susceptibility at 20°	—	—	$-0·72 \times 10^{-6}$	$-0·64 \times 10^{-6}$
Heat of dissociation k. cal./mol	102·5	104·5	—	—

The D_2 molecule, like H_2 (p. 288), exists in ortho and para forms. The equilibrium mixture at room temperature is 2 ortho to 1 para; at low temperatures it is almost entirely ortho (H_2 is para). The mobilities of ions in D_2O are distinctly smaller than in H_2O, *e.g.* for K^+ at 18° these are 64·2 for H_2O and 54·5 for D_2O. The solubilities of some salts in D_2O are smaller, of others greater, than in H_2O. Deuterium oxide is very hygroscopic and should not be exposed to moist air.

The density, refractive index, and critical solution temperature for phenol, etc., are used to determine the amount of D_2O in water, the density method being most sensitive; allowance is made for possible variation in heavy oxygen (^{18}O) content (Longsworth, *J.A.C.S.*, 1937, **59**, 1483; Swift, *ibid.*, 1939, **61**, 198). The D_2 content of hydrogen gas is best determined from the thermal conductivity, although the mass spectrograph is more suitable for very small concentrations (below 1 p.c.).

In mixtures of H_2 and D_2, and of H_2O and D_2O, as well as other compounds, *exchange reactions* of H and D atoms occur and hence, owing to the reactions :

$$H_2 + D_2 \rightleftharpoons 2HD \quad \text{and} \quad H_2O + D_2O \rightleftharpoons 2HDO$$

the molecules HD and HDO are also present. The equilibrium constants of these reactions have been determined or calculated. Deuterium has been used to determine the mechanism of reactions involving exchange of hydrogen atoms.

Every hydrogen compound could have a corresponding deuterium compound, and many of these have been prepared. The acid DCl is formed from the elements, and DF by the reaction $D_2 + 2AgF = 2Ag + 2DF$ at 110°. " Heavy ammonia " ND_3 is formed from D_2O and Mg_3N_2 and combines with many salts (Hart and Partington, *J.C.S.*, 1943, 104). Deuteromethane CD_4 is obtained from D_2O and Al_4C_3, and deuteroacetylene C_2D_2 from D_2O and CaC_2. The acids DNO_3, D_2SO_4 and D_3PO_4 are formed by dissolving the anhydrides in D_2O. The exchange reaction $NH_4Cl + 2D_2O \rightleftharpoons ND_4Cl + 2H_2O$ occurs in solution, and has been used to remove small amounts of deuterium from water. Many organic compounds in which hydrogen is partly or wholly replaced by deuterium have been prepared.

Association (*e.g.* of DF) is greater with deuterium compounds than with the corresponding hydrogen compounds (*e.g.* HF).

The melting and boiling points in °C. of some hydrogen and deuterium compounds are shown below :

	m.p.°	b.p.°		m.p.°	b.p.°
NH_3	−77·9	−33·3	HI	−50·9	−35·6
ND_3	−73·6	−31·1	DI	−51·7	−36·1
HF	—	20	HCN	−14	25·4
DF	—	18·7	DCN	−12	26·1
HCl	−111·4	−85·0	CH_3COOH	16·6	—
DCl	−114·9	−81·5	CD_3COOD	15·8	—
HBr	−86·9	−66·8	C_6H_6	5·5	80·12
DBr	−87·4	−66·8	C_6D_6	6·8	79·4

The crystal hydrate $CuSO_4,5D_2O$ is greener in colour than $CuSO_4,5H_2O$. The dissociation pressures of deuterates (compounds of D_2O) and deuterammines (compounds of ND_3) with salts are somewhat smaller at a given temperature than those of corresponding hydrates and ammines (compounds of NH_3). The ionic product of heavy water at 25° is $[D^+]\,[OD^-] = 1{\cdot}95 \times 10^{-15}$, that of ordinary water being $[H^+]\,[OH^-] = 1{\cdot}0 \times 10^{-14}$.

CHAPTER XII

THE ALKALI METALS

First Group Metals

Group I of the Periodic System contains two groups of metals, (i) the *even series* or sub-group *a*, of the **alkali metals** (No. 87 is unknown), and (ii) the *odd series* or sub-group *b*, comprising **copper, silver** and **gold.** The odd and even series show startling differences, and would never have been brought into the same group on purely chemical grounds.

The alkali metals are the most strongly electropositive elements known, the positive character increasing with atomic weight from lithium to caesium. The elements of the odd series have a much less pronounced electropositive character and this decreases with rise of atomic weight, gold being among the most weakly electropositive metals. The alkali metals oxidise with the greatest ease and decompose water violently; copper oxidises in air only appreciably on heating and decomposes water only at a very high temperature, whilst silver and gold are "noble" metals, which can be heated to redness in air without oxidation. Lithium shows marked differences from the other alkali metals and in many ways resembles magnesium, its neighbouring element in Group II.

The standard electrode potentials (p. 115) in volts are:

Li	Na	K	Rb	Cs
−3·02	−2·712	−2·922	−2·99	−3·02
	Cu	Ag	Au	
	+0·345	+0·7995	+1·42	

Although lithium is anomalous in this respect (since it is chemically less electropositive than the other alkali metals), the other alkali metals increase in electropositive character with atomic weight, the opposite being the case for copper, silver and gold in the compounds of Cu^{II}, Ag^{I} and Au^{III}.

The alkali metals are all univalent in simple compounds and salts, but show covalencies of 4 and 6 in some compounds (p. 296). Copper shows ordinary valencies of 1 and 2 and sometimes 3; silver valencies of 1 and sometimes 2 and 3, and gold valencies of 1 and 3 of more nearly equal stability. Whilst the alkali metals show no tendency to form complex compounds, this is very marked with copper, silver and gold, which form both cation, *e.g.* $[Cu(NH_3)_4]SO_4$, and anion, *e.g.* $K[Ag(CN)_2]$, complexes, and these elements also show a marked tendency to form covalent compounds even with the strongly electronegative halogens, which tend to remove electrons from metal atoms to form positive ions. Cuprous and argentous chlorides (CuCl, AgCl) have non-ionic lattices, and fused cuprous chloride is not a good conductor (although fused silver chloride is), and in the vapour state the molecule is Cu_2Cl_2.

The typical (in Mendeleéff's sense, p. 178) *oxides* M_2O of the alkali metals are very stable and do not dissociate even at high temperatures; cuprous oxide Cu_2O is also stable, but silver oxide Ag_2O and especially aurous oxide Au_2O are easily decomposed by heat. The alkali *hydroxides* can be fused without loss of water, but those of copper and gold easily lose water, and silver hydroxide is so unstable that it is formed only under very special conditions, the oxide usually appearing instead.

The oxides, hydroxides, sulphides, carbonates and phosphates of alkali metals are all soluble (except the carbonate and phosphate of lithium, which are sparingly soluble), but those of copper, silver and gold, when they exist, are sparingly soluble. The halides of alkali metals are soluble, but cuprous, argentous and aurous halides are insoluble; cupric and auric halides are soluble.

The heats of formation (k. cal. evolved) for some corresponding compounds are:

	K	Cu	Ag	Au
MCl	104·3	34·3	30·3	8·3
MBr	94·1	26·7	23·8	3·4
MI	78·9	17·8	14·9	−0·2
M_2O	86·2	38·5	6·95	$[Au_2O_3 - 11]$

The Alkali Metals

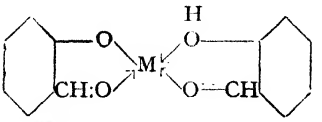
The **alkali metals** are **lithium, sodium, potassium, rubidium** and **caesium**; the radical **ammonium** NH_4, known as an amalgam with mercury, forms compounds very like those of alkali metals.

The *physical properties* of the alkali metals are shown below:

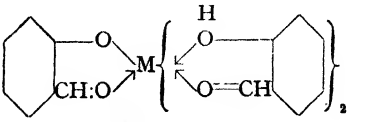
	Lithium	Sodium	Potassium	Rubidium	Caesium
Atomic number	3	11	19	37	55
Electron configuration	2·1	2·8·1	2·8·8·1	2·8·18·8·1	2·8·18·18·8·1
Density at 0°	0·5	0·9723	0·859	1·525	1·903
Atomic volume	12·9	23·7	45·5	56·1	69·8
Melting point	180°	97·9°	63·50°	39·0°	28·45°
Boiling point	1336°	882·9°	757·5°	700°	670°
Colour of vapour	?	purple, yellow fluorescence	green	greenish-blue	blue

The alkali metals displace all other metals from their salts, and are the only metals forming stable solid bicarbonates $MHCO_3$. They nearly always show electrovalency, but a few covalent compounds are known, *e.g.* sodium methyl CH_3Na formed by the action of sodium on mercury methyl in dry benzene: $2Na + Hg(CH_3)_2 = Hg + 2CH_3Na$. The vapour density of sodium chloride corresponds with NaCl (Nernst, 1903). The alkali metal atoms have a single valency electron in the outer shell which is easily lost and the next lower group of electrons (2 in lithium, 8 in the other alkali metals) is very stable, so that the ion is always univalent.

They show *covalencies* of 4 and 6 in a few compounds, *e.g.* with salicylaldehyde:



M = Li, Na, K, Rb, Cs.



M = K, Rb, Cs.

The alkali metal vapours are largely monatomic, but sodium vapour (mol. wt. 24–26) contains some Na_2 molecules (Rodebush and Walters, *J.A.C.S.*, 1930, **52**, 2654). In solution in tin, sodium is monatomic. The metals all crystallise in body-centred cubic lattices. They form salt-like **hydrides** MH and **halides** MX. The **basic oxides** are M_2O, but higher oxides, Li_2O_2, Na_2O_2 and Na_2O_3, and M_2O_2, M_2O_3, and MO_2 with K, Rb and Cs, are known. The metals are very reactive and combine directly with halogens and sulphur, and lithium with nitrogen. Lithium reacts rapidly with water and sodium violently, but the hydrogen liberated does not inflame; potassium, rubidium and caesium react with increasing violence and the hydrogen inflames.

Plant and wood ashes containing potassium carbonate were used as detergents in antiquity, and native sodium carbonate (*natron*) from lakes by the ancient Egyptians in embalming and in making glass (Partington, *Origins and Development of Applied Chemistry*, 1936). Pliny mentions the caustification of alkalis by boiling with quicklime as known in Egypt. Potash (from wood ashes) and soda (from natron or the ashes of marine plants) were distinguished by tests by Duhamel in 1736 and by Marggraf in 1757. The chemical nature of the "mild" alkalis (carbonates) as compounds formed from the "caustic" alkalis (hydroxides) and "fixed air" (carbon dioxide) was established by Joseph Black (*Dissertation on Magnesia*, 1754).

The alkali metals potassium (which he first called "potasium") and sodium were isolated in 1807 by the electrolysis of the fused hydroxides by Davy (*Phil. Trans.*, 1808, **98**, 1; *Alembic Club Reprint* No. 6), who determined their densities by flotation in a mixture of oil of sassafras and naphtha. Gay-Lussac and Thenard in 1808 obtained the metals by the action of red-hot iron on the fused hydroxides, finding that hydrogen was evolved and thus showing that caustic alkalis are hydroxides.

EXPT. 1.—Heat a mixture of powdered caustic soda and iron filings in a hard glass tube with a jet. Hydrogen is evolved and may be kindled.

Lithium was discovered by Arfvedson in 1817, the metal being isolated by Davy in 1818 and Bunsen and Matthiessen in 1855. Caesium and rubidium were discovered by the spectroscope by Bunsen and Kirchhoff in 1860 and 1861, respectively, caesium in a mineral water of Dürkheim and rubidium in the lithium mineral lepidolite.

Occurrence of Sodium and Potassium

Sodium compounds occurring naturally in large amounts are the *chloride* NaCl (common salt), *carbonate* Na_2CO_3, *sulphate* Na_2SO_4 and double sulphates with calcium, the *borate* $Na_2B_4O_7$ and double borates, and the *nitrate* $NaNO_3$. Sodium also occurs in some rocks such as *albite* or sodium felspar $NaAl(SiO_3)_3$. It is found in all parts of animals but in plants it plays only a minor role as compared with potassium.

Potassium, although widely distributed and occurring to about the same extent (2·33 p.c. overall) as sodium, is less accessible. Comparatively few workable *deposits of potassium salts* occur; the principal are at Stassfurt in Saxony and at Mulhouse in Alsace. There are smaller deposits in Cardona (Spain), Eastern Galicia, Kalusz (Poland), the Dead Sea, Tunis, Elton Lake (Urals), Searle's Lake (California), and Carlsbad (New Mexico). The main Stassfurt mineral is *carnallite* $KMgCl_3,6H_2O$.

Potassium occurs in some primary rocks such as granite (1·7–3·1 p.c. K), which contain it as potassium or *orthoclase felspar* $KAl(Si_3O_8)$, *leucite* $KAl(SiO_3)_2$, and *potash mica*, usually formulated $KH_2Al_3(SiO_4)_3$. In weathering by water and atmospheric carbon dioxide, these form clay and the soluble potassium salts are retained in the soil, probably by base-exchange for sodium in zeolites (p. 426).

According to Dyer (1894) the minimum percentage of soluble K_2O in fertile soil is 0·01; the mean available content of British soils is 0·015 p.c. Trees remove annually 1·25 lb. of K_2O per acre, other plants more. In order to maintain the fertility of the soil, potassium compounds must be supplied.

Blood serum contains 0·022 p.c. of potassium and 0·32 p.c. of sodium. In the milk of carnivora sodium and potassium occur in equivalent amounts; in that of herbivora and in human milk potassium predominates (3·5 : 1). (The ratio in plants is variable.) Some potassium carbonate is made from raw wool washings, which are evaporated and the residue calcined; about 5 parts of potassium carbonate remain per 100 of wool.

Potassium salts occur in the sea and are absorbed in marine plants, from the ash (*kelp*) of which they may be extracted. Sugar beets absorb considerable amounts of potassium salts from the soil, which accumulate in the molasses (*vinasse* or *schlempe*). This is burnt, leaving a residue of potassium carbonate.

The Norsk Hydro. Co. extract potassium salts from sea water by precipitating with dipicrylamine (hexanitrodiphenylamine) which recovers 70 p.c. of the content of 0·4–0·45 kg. K_2O per cu. m.; the precipitate is decomposed with nitric acid to make potassium nitrate.

Some potassium compounds are recovered from blast furnace and cement kiln dusts, and from some petroleum brines.

Potassium and rubidium are feebly radioactive, emitting β-rays. The activity of potassium is only $\frac{1}{1000}$ that of uranium. The radioactive isotope, which can be partly separated by distillation, is ^{40}K, with the abundance ratio $^{39}K : {}^{40}K = 8500 : 1$. Another isotope is ^{41}K, with the abundance ratio $^{39}K : {}^{41}K = 14 : 1$, which is somewhat smaller in some plant ashes, especially kelp (Brewer, 1935–6). Lithium, sodium and caesium are not radioactive.

Metallic Sodium and Potassium

Metallic sodium is made electrolytically by the process used in its discovery by Davy in 1807. Fused sodium hydroxide is electrolysed and the sodium deposits on the cathode.

The hydroxide ions discharged on the anode decompose: $4OH = O_2 + 2H_2O$, and the water formed reacts with some sodium at the cathode, evolving hydrogen (Wallace and Fleck, *J.C.S.*, **1921, 119**, 1839): $2Na + 2H_2O = 2NaOH + H_2$. The total reaction is $2NaOH = (2Na + H_2)$ cathode $+ O_2$ anode.

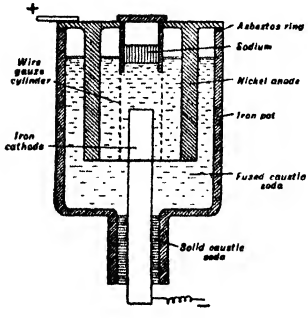


FIG. 170.—Castner sodium cell.

In the **Castner process** (1890) caustic soda is fused by gas-burners in a cylindrical iron pot (Fig. 170) at a temperature not higher than 330°. A cylindrical iron cathode passes through the base and is sealed by solid caustic soda. The anode is a nickel cylinder in electrical connection with a wire gauze cylinder surrounding the cathode. The metal rises from the cathode and floats on the surface inside a small metal receptacle with a lid. It is removed by a wire gauze spoon, which allows the fused caustic soda to flow away but retains the sodium. The latter is sent out in the form of thick rods sealed up in tin cans.

Sodium is also made by the electrolysis of fused sodium chloride, alone or mixed with potassium or calcium chloride or sodium fluoride, which lower the melting point to about 600° (sodium chloride melts at 801° and sodium boils at 883°).

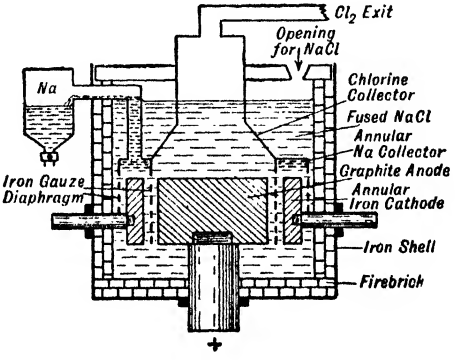


FIG. 171.—Downs sodium cell.

In the **Downs cell** (Fig. 171) a central carbon anode is surrounded by an annular iron cathode separated from it by metal gauze. The light sodium rises from the cathode into an annular space from which it runs off; the chlorine from the anode passes through a conical collecting hood.

violently with water: $Na_2O + H_2O = 2NaOH$; it does not react with carbon dioxide at room temperature but burns in it on heating: $Na_2O + CO_2 = Na_2CO_3$.

Sodium peroxide Na_2O_2 (Gay-Lussac and Thenard, 1811) is formed when the metal burns in excess of air or oxygen. It is manufactured by heating sodium in aluminium trays in a current of purified air at 300° in iron pipes, or by burning sodium in air in a revolving iron cylinder to Na_2O and oxidising this to Na_2O_2 in a second revolving drum in a current of air.

Sodium peroxide is pale yellow, becoming white on exposure to air from formation of hydroxide and carbonate. When very strongly heated it evolves oxygen. A solution may be prepared by adding the powder in small quantities to a well-stirred mixture of ice and water, a crystalline hydrate $Na_2O_2,8H_2O$ being formed. The solution is strongly alkaline owing to hydrolysis:

$$Na_2O_2 + 2H_2O \rightleftharpoons 2NaOH + H_2O_2,$$

and on warming evolves oxygen. Carbon dioxide decomposes sodium peroxide with evolution of oxygen, hence the solid has been used for purifying air in confined spaces (*e.g.* in submarines). Sodium peroxide is an oxidising agent: the solution converts chromic hydroxide into sodium chromate and the fused oxide oxidises chrome-ironstone (FeO,Cr_2O_3) into ferric oxide and sodium chromate. The fused peroxide attacks silver, but may be used in nickel crucibles (cf. Wallace and Fleck, *J.C.S.*, 1921, **119**, 1839).

If a little sodium peroxide mixed with sawdust is placed on filter paper and moistened with water, the mass inflames. If mixed with pieces of recently ignited charcoal and heated in a covered porcelain crucible to 300°–400°, a violent reaction occurs and metallic sodium condenses on the lid of the crucible (Bamberger, 1898): $3Na_2O_2 + 2C = 2Na_2CO_3 + 2Na$. Glacial acetic acid inflames when the peroxide is dropped into it.

Sodium peroxide forms with absolute alcohol at 0° a white powder of **sodium hydrogen peroxide** Na·O·O·H or $NaHO_2$ (Tafel, 1894; d'Ans and Friederich, 1912):

$$Na_2O_2 + EtOH = NaOEt + NaO{\cdot}OH.$$

It explodes on heating, evolving oxygen: $2NaO(OH) = 2NaOH + O_2$. A stable compound $2NaHO_2,H_2O_2$ is formed on mixing 30 p.c. hydrogen peroxide with sodium ethoxide (NaOEt) and absolute alcohol, or by the action of an ether solution of H_2O_2 on sodium. Potassium forms $2KHO_2,H_2O_2$.

Potassium burns in a good supply of air or oxygen mainly to the chrome-yellow **potassium dioxide** KO_2, which is a powerful oxidising agent: it oxidises carbon monoxide to dioxide at 100°.

Alkali Hydroxides

Sodium hydroxide (*caustic soda*) NaOH is obtained pure by adding small bits of clean sodium or sodium wire from a press to previously boiled and cooled distilled water in a silver dish, evaporating the solution, and fusing. Pieces of sodium may also be added to water covered with a layer of ether, when the metal reacts slowly in the ether layer (Cornog, *J.A.C.S.*, 1921, **43**, 2573).

Caustic soda is made technically:

(1) By the **electrolysis** of a solution of common salt (p. 773). In the Castner-Kellner or the Solvay cell pure sodium hydroxide solution is formed from the sodium amalgam and water; in cells in which the brine is not completely separated from the sodium hydroxide solution the latter also contains undecomposed salt, say 12 p.c. of each. It is evaporated in a vacuum evaporator with an arrangement for removing the common salt which separates. When it contains 50 p.c. of NaOH only 1 p.c. of NaCl remains. The solution is then evaporated in an iron pot over a fire until fused caustic soda remains.

(2) In the **Löwig process** a mixture of sodium carbonate (*soda-ash*) and ferric oxide is heated to bright redness in a revolving furnace, when sodium ferrite $NaFeO_2$ is formed. This is cooled, broken up and thrown into hot water, when sodium hydroxide solution and ferric oxide (which is used again) are formed:

$$Na_2CO_3 + Fe_2O_3 = 2NaFeO_2 + CO_2$$
$$2NaFeO_2 + H_2O = Fe_2O_3 + 2NaOH.$$

(3) By **causticising** a 20 p.c. solution of sodium carbonate by heating with slaked lime in iron pans fitted with agitators:

$$Na_2CO_3 + Ca(OH)_2 \rightleftharpoons 2NaOH + CaCO_3.$$

The reaction is reversible, and as the concentration of sodium carbonate decreases the solubility of calcium carbonate increases, since the CO_3'' ions, which depress the solubility of the calcium carbonate, are removed. At the same time the increasing concentration of OH' ions depresses the solubility of the calcium hydroxide. A state of equilibrium is reached when the solubilities of the calcium carbonate and hydroxide become equal, when $[OH']^2/[CO_3''] = K$.

With increasing concentration the equilibrium shifts from the hydroxide to the carbonate side of the equilibrium, since $[CO_3'']$ is involved as the first power but $[OH']$ as the square. Caustification is more complete (99 p.c.) in dilute solutions (normal). In practice 91–92 p.c. of caustification is obtained. Better results could be obtained with strontium and barium hydroxides, as these are more, and the carbonates less, soluble than those of calcium, but they are too expensive for technical use. The double salts *gaylussite* $Na_2CO_3,CaCO_3,5H_2O$ (which occurs native) and *pirssonite* $Na_2CO_3,CaCO_3,2H_2O$, may be formed by the action of concentrated sodium carbonate solution on calcium carbonate, but they are probably unstable above 80° (Goodwin, *J.S.C.I.*, 1926, **45**, 360T; Bury and Redd, *J.C.S.*, 1933, 1160).

The granular calcium carbonate formed as a by-product may be reconverted into quicklime by heating, or sold for agricultural lime, " stone-dusting " in coal mines to prevent explosions of coal dust, and when dried and air-separated for other purposes.

The commercial sodium hydroxide is fused and poured into iron drums, in which it solidifies. It contains about 1 p.c. of water. For laboratory use it is cast into sticks or made into pellets, flakes, " petals " or powder.

Sodium hydroxide is a white slightly translucent solid with a fibrous texture, s.g. 2·13. It fuses at 318·4° and at about 1300° dissociates:

$$2NaOH \rightleftharpoons 2Na + H_2 + O_2.$$

When exposed to air it first deliquesces from absorption of moisture and a little carbon dioxide, forming a saturated solution. This slowly solidifies from absorption of carbon dioxide, when the carbonate, which is sparingly soluble in the solution, is formed. Potassium hydroxide after deliquescence does not resolidify, since potassium carbonate is readily soluble. For this reason concentrated potash is used in gas analysis to absorb carbon dioxide, since it does not deposit solid which would choke the apparatus. Caustic soda and potash are powerful cauteries.

Potassium hydroxide KOH, m.p. 360·4°, is made in similar ways to sodium hydroxide and has similar properties. It is used for making soft-soap (potassium salts of fatty acids). A pure product is made by adding powdered potassium sulphate to a hot saturated solution of barium hydroxide :

$$K_2SO_4 + Ba(OH)_2 = 2KOH + BaSO_4,$$

decanting the clear solution and evaporating in a silver dish ; or by the action of water on potassium amalgam. The commercial hydroxide may be purified (Berthollet, 1786) by dissolving in alcohol, decanting the solution from chloride, carbonate and sulphate, evaporating in a silver dish and fusing (" pure by alcohol ").

Sodium hydroxide forms hydrates with 7, 5, 4, 3·5, 3·11, 2 (m.p. 12·7°) and 1 (m.p. 64°) H_2O, and potassium hydroxide with 4 (m.p. − 32·7°), 2 (m.p. 35·5°), $1\frac{1}{2}$ and 1 (m.p. 143°) H_2O (Pickering, *J.C.S.*, 1893, **63**, 890). The hydroxides are very soluble and dissolve with considerable evolution of heat. The solubilities in g. MOH per 100 g. of water, in equilibrium with the stable hydrate, are (Pickering, 1893) :

	0°	10°	20°	40°	60°	80°	110°
NaOH -	42	51·5	109	129	174	313	365
KOH - -	99·2	106·1	112·7	136·9	150	163·4	201·3

The densities of the solutions (D_4^{15}) are (Pickering, 1893) :

p.c. - -	5	10	15	20	30	40	50
NaOH - -	1·056	1·111	1·166	1·222	1·331	1·434	1·530
KOH -	1·045	1·092	1·140	1·188	1·291	1·399	1·514

Alkali Halides

Sodium and potassium *halides*, all anhydrous MX compounds forming cubic crystals, are :

NaF, m.p. 993°, b.p. 1695°, rather sparingly soluble ; $NaHF_2$, decomposed on heating : $NaHF_2 = NaF + HF$.

NaCl, m.p. 801°, b.p. 1440° ; forms $NaCl,2H_2O$.

NaBr, m.p. 766°, b.p. 1396° ; deliquescent, forms $NaBr,2H_2O$ and $NaBr,5H_2O$.

NaI, m.p. 665°, b.p. 1300° ; deliquescent, forms $NaI,2H_2O$ and $NaI,5H_2O$.

KF, m.p. 846°, not deliquescent, KHF_2 (stable), KH_3F_4 and KH_5F_6 (unstable).

KCl, m.p. 775°, KBr, m.p. 740°, KI, m.p. 680°, all non-deliquescent. The solubilities of potassium iodide are :

	0°	10°	20°	40°	100°
g. per 100 g. H_2O -	127·5	136	144	160	208

Potassium and sodium chlorides form mixed crystals at higher temperatures, but these separate at about 400°.

Sodium chloride occurs in cubic crystals as *rock salt* or *halite*. The crystals are colourless when pure, but are often tinged by impurities, yellow, brown, or sometimes blue (perhaps due to metallic sodium ; Wöhler, 1905). Rock salt mostly occurs in large masses more or less coloured with impurities, *e.g.* iron, and has a cubic cleavage.

The richest English deposits (which were worked by the Romans) are around Northwich in Cheshire. There are large deposits in Stassfurt (Germany), Orenberg (Russia), Wieliczka (Poland)—where there is an underground town—Cadorna (Spain)—where there are two hills of rock salt each nearly a mile in circumference—in Canada, India, and in the U.S.A. in Michigan, New York, Ohio, Kansas, Louisiana, Texas and California. A Texas salt dome is said to be 3000 ft. thick. More or less concentrated (say 25 p.c.) *brines* are also found in most of these places, at Droitwich, in the Dead Sea (22–23 p.c.), Salt Lake (Utah), etc. A saturated solution contains 35·78 parts of salt in 100 of water at 15°, or 26 p.c. The solubility increases only slowly with temperature (Fig. 36) :

	0°	10°	20°	30°	50°	70°	90°	100°	107°
g./100 g. H_2O -	35·57	35·69	35·82	36·08	36·67	37·51	38·52	39·22	39·65

The s.g. of the solution at 15° is :

p.c. salt - -	2	5	10	15	20	25	26·8
s.g. - -	1·0137	1·0355	1·0726	1·1105	1·1497	1·1904	1·2055

In fused mercuric chloride the molecular weight of sodium chloride corresponds with NaCl (Beckmann, 1907).

An analysis of Northwich brine is as follows in p.c. :

Sodium chloride - - -	25·790	Calcium chloride - - -	0·044
Calcium sulphate - - -	0·450	Calcium carbonate - -	0·018
Magnesium chloride - -	0·093	Water - - - -	73·605

The brine is evaporated in open rectangular iron pans over a fire, or in vacuum pans, the steam from one pan passing to the heating element in the next, which is under lower pressure. To prevent scaling, the calcium and magnesium salts are first precipitated with sodium carbonate. The more slowly the evaporation proceeds, the larger are the crystals deposited. The different grades according to fineness are : *fine* or *table salt*, *manufacturer's salt*, *fishery salt*, and *bay salt* (usually in the form of floating " hoppers," or cubes with hollow stepped faces).

In warm climates (*e.g.* in the South of France, Spain, California, Utah) sea water is evaporated in large flat ponds called *salt meadows* by the heat of

the sun; the salt so made is called *solar salt*. The mother-liquor, called *bittern*, contains the magnesium salts and bromides of the sea water.

Sodium chloride is purified in the laboratory by precipitating a saturated solution with hydrogen chloride gas (passed in by an inverted funnel), filtering, drying, and heating in a dish. Potassium chloride is removed by repeated crystallisation from water.

By cooling a saturated solution at $-10°$, or cooling a hot saturated solution in hydrochloric acid, the crystal hydrate $NaCl,2H_2O$ deposits (p. 64; Adams and Gibson, *J.A.C.S.*, 1930, **52**, 4252).

Common salt is used in flavouring and preserving, salting-out soap, regenerating water softeners (p. 676), making alkali and chlorine, melting snow and ice on roads (when a solution liquid down to the eutectic temperature is formed; p. 64), and in salt-glazing stoneware. In salt-glazing, moist salt is thrown into the furnace in which the goods are fired, and the vapour in presence of steam hydrolyses: $NaCl + H_2O = NaOH + HCl$. The alkali forms a fusible silicate glaze with the clay.

The hydrolysis may be shown by fusing salt in a platinum dish and adding water, which becomes spheroidal. The drop of water is poured on blue litmus paper, which turns red. The salt in the dish is cooled, dissolved in water and poured on red litmus paper, which turns blue (Emich, *Ber.*, 1907, **40**, 1482).

Potassium chloride occurs in cubic crystals as *sylvine*. It is easily soluble in water, the solubility increasing almost linearly with temperature: 0° 28, 15° 32·7, 100° 56·5 g./100 g. H_2O. It is made from carnallite and used as a fertiliser.

Carnallite, found in the Stassfurt deposits, is $KMgCl_3,6H_2O$, and when pure contains 14·0 p.c. of potassium. It is usually pink from ferric oxide. *Sylvite*, a mixture of sodium and potassium chlorides, occurs in Galicia and Alsace (35–40 p.c. KCl in the upper and 24–32 p.c. in the lower parts). The Stassfurt *kainite* $KCl,MgSO_4,3H_2O$ is not much worked.

To prepare potassium chloride the carnallite is fused, when nearly pure solid potassium chloride separates leaving fused magnesium chloride hexahydrate: $KCl,MgCl_2,6H_2O \rightleftharpoons KCl + MgCl_2,6H_2O$. The potassium chloride is recrystallised. Usually the carnallite is treated with mother-liquor from the crystallisations. On heating the paste of potassium chloride and saturated solution of magnesium chloride a clear solution is obtained, from which on cooling 80 p.c. of the potassium chloride is deposited (van't Hoff and Meyerhoffer, *Z. phys. Chem.*, 1899, **30**, 64).

Alkali metal polyhalides.—Iodine is more soluble in alkali iodide solution than in water, and the brownish-red solution contains the polyiodide ion I_3'. Many *solid* polyiodides and mixed halides are known, mostly anhydrous but potassium tri-iodide only as the hydrate KI_3,H_2O (Grace, *J.C.S.*, 1931, 594). The methods of preparation include (i) the direct addition of halogen ($KICl_2 + Cl_2 = KICl_4$) and (ii) halogen or halogen compound displacement ($CsBr_3 + I_2 = CsIBr_2 + IBr$; $CsICl_2 + 2IBr = CsIBr_2 + 2ICl$) (Cremer and

Duncan, *J.C.S.*, 1931, 1857 ; 1933, 181). Apart from the actual preparation of the solids, the complex ions may be detected in solution by the usual methods.

In a method used by Abegg and Hamburger (1906) a fairly concentrated solution of iodine in benzene is shaken with solid MI. If two *solid* phases are present, *e.g.* MI_x and MI, the iodine concentration in the liquid phase will be constant on addition of iodine until there is only one solid phase MI_x, when it begins to alter. The solid is analysed at this point.

Some types of polyhalides are :

(1) MX_2 : known only as $NaI_2,3H_2O$ (Cheesman, Duncan and Harris, *J.C.S.*, 1940, 837).

(2) MX_3 : a common type, known in tri-iodides of K (hydrated), Rb, Cs, NH_4, Tl^I ; and in mixed halides $MICl_2$ (K, Rb, Cs, NH_4), CsI_2Cl (the only one of this type), $CsIBr_2$, KIBrCl, CsIBrF, etc.

(3) MX_4 : known as $NaI_4,2H_2O$ (Cheesman, etc., *loc. cit.*) and CsI_4 (Grace, *J. Phys. Chem.*, 1933, **37**, 347 ; Foote, etc., *ibid.*, 21), which may be Cs_2I_8.

(4) MX_5 : known in $NaI_5,2C_6H_5NO_2$, and the very stable orange-red mixed halides $MICl_4$ (Li, Na, K, Rb, Cs, NH_4), also $MICl_3F$ (Booth, etc., *J. Phys. Chem.*, 1932, **36**, 347, 2779 ; *J.A.C.S.*, 1932, **54**, 2561).

(5) MI_6 : known in $2KBr_6,3H_2O$ (Harris, *J.C.S.*, 1932, 1694).

In these compounds the heavy halogen is multivalent (Lowry, etc., *J.C.S.*, 1931, 1092), the $[Cl—I—Cl]^-$ ion being linear and the ICl_4' ion square with four chlorines at the corners (Wyckoff, 1920 ; Mooney, 1935–8).

Alkali Carbonates

Sodium carbonate, Na_2CO_3, was until about 1800 made from the ash (*barilla*) of seashore plants (*Chenopodium*, *Salicornia*, *Salsola*, etc.). Stahl in 1703 knew that alkali can be made from common salt, and Scheele in 1771 decomposed salt by boiling the solution with lead oxide :

$$2NaCl + 4PbO + H_2O = 2NaOH + PbCl_2,3PbO,$$

and found that a mixture of moist salt and quicklime slowly formed an efflorescence of sodium carbonate, but the first successful process for making sodium carbonate from common salt was patented by Nicolas Leblanc (or Le Blanc) in 1787.

In the **Leblanc process**, largely worked at one time but now almost obsolete, sodium sulphate or *salt-cake*, made by heating salt with concentrated sulphuric acid (p. 314) :

$$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl,$$

is heated in a revolving cylindrical iron furnace with coal and limestone, when sodium carbonate and calcium sulphide are formed :

$$Na_2SO_4 + 2C = Na_2S + 2CO_2$$
$$Na_2S + CaCO_3 = Na_2CO_3 + CaS.$$

The sodium carbonate is extracted with water, the impure insoluble calcium sulphide (*alkali waste*) being treated by the Chance-Claus process (p. 689) to recover the sulphur.

A successful process, which is still in use, is the **ammonia-soda process** (sometimes called the *Solvay process*). This makes use of the interaction of a concentrated solution of sodium chloride, ammonia and carbon dioxide, when sparingly soluble sodium hydrogen carbonate (bicarbonate) is precipitated. An equilibrium is set up, the reaction being incomplete (Fedotiev, *Z. phys. Chem.*, 1904, **49**, 162; Toporescu, *Compt. rend.*, 1922, **174**, 870; Neumann and Domke, *Z. Elektrochem.*, 1928, **34**, 136; Findlay, *Phase Rule*, 1938, 298; a different account is given by Mason, *Chem. Ztg.*, 1914, **38**, 513):

$$NaCl + NH_4HCO_3 \rightleftharpoons NaHCO_3 + NH_4Cl.$$

The process was proposed by Fresnel about 1810 (Lucion, *Chem. Ztg.*, 1889, **13**, 627) and worked for a year or two in Scotland by John Thom in 1836 (Mond, *J.S.C.I.*, 1885, **4**, 527; Smith, *ibid.*, 1887, **6**, 699). Dyar and Hemming took out a patent for it in 1838 and worked it in London for a short time; it was also worked near Paris in 1855 by Schloesing and Rolland, who gave a full account of it (*Ann. Chim.*, 1868, **14**, 5). Ernest Solvay's first patent was taken out in 1861, but his process was first worked near Nancy in 1872. It was operated from 1874 by John Brunner and Ludwig Mond at Winnington, near Northwich in Cheshire, where it is still worked by Imperial Chemical Industries, Ltd. It is worked at Dombasle in Lorraine and in the United States at Syracuse, N.Y., but is tending to give way to electrolytic methods.

In the ammonia-soda process a nearly saturated solution of NaCl, freed from the calcium and iron, and most of the magnesium, salts of the original brine is taken, and ammonia gas passed into it in an iron tower fitted with bubblers. Carbon dioxide is then bubbled under pressure into the ammoniacal brine in an iron *carbonating tower* (Fig. 172), 6 ft. in diameter and 70–90 ft. high, fitted with bubblers and cooled below by iron pipes through which cold water circulates. The carbon dioxide first converts the ammonia into carbonate:

$$2NH_3 + H_2O + CO_2 = (NH_4)_2CO_3,$$

and then tends to convert this into bicarbonate:

$$(NH_4)_2CO_3 + H_2O + CO_2 \rightleftharpoons 2NH_4HCO_3.$$

As ammonium bicarbonate is formed it reacts with the sodium chloride, giving sodium bicarbonate and ammonium chloride:

$$NH_4HCO_3 + NaCl \rightleftharpoons NaHCO_3 + NH_4Cl.$$

The sodium bicarbonate is only slightly soluble in brine and is nearly all precipitated, whilst the ammonium chloride remains in solution. Only two-thirds of the common salt is converted into bicarbonate, since the reaction is reversible, and one-third of the salt remains. The sodium bicarbonate is filtered in rotary vacuum filters and washed with a little cold water. The mother-liquor passes to the ammonia-stills in which it is heated with lime to recover the ammonia.

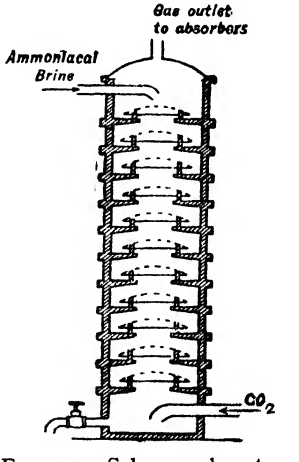


FIG. 172.—Solvay carbonating tower.

The sodium bicarbonate is heated in closed tubular iron pans with scrapers (*Thelen pans*). Carbon dioxide is evolved: $2NaHCO_3 = Na_2CO_3 + H_2O + CO_2$.

This " roaster " gas is mixed with scrubbed gas from limekilns where the limestone is burnt mixed with coke to produce lime for the ammonia-stills, and the mixed gas is passed to the carbonating towers. Sodium carbonate or *soda-ash* issues from the calcining pan ; it usually contains only a little sodium chloride derived from the mother-liquor left in the bicarbonate on the filters.

Anhydrous sodium carbonate is a white amorphous powder, m.p. 852°, decomposing slightly above 270° : $Na_2CO_3 = Na_2O + CO_2$, and appreciably on fusion in a porcelain crucible (when silicate is formed) (Ferguson, *J.S.C.I.*, 1905, **24**, 781). The powder aggregates in moist air from formation of hydrates ; on adding to water a solid mass of hydrate is formed with evolution of heat (21·8 k. cal. for the formation of $Na_2CO_3,10H_2O$), and the solution is alkaline owing to hydrolysis :

$$Na_2CO_3 + H_2O \rightleftharpoons NaHCO_3 + NaOH, \text{ or } CO_3'' + H_2O \rightleftharpoons HCO_3' + OH'.$$

Mols/lit. - - -	0·19	0·094	0·0477	0·0238
Hydrolysis p.c. at 24·2° -	2·12	3·17	4·87	7·10

On evaporating the solution and cooling, large monoclinic crystals of *washing-soda* $Na_2CO_3,10H_2O$ are deposited. These dissolve with absorption of heat. They effloresce in air to a white powder of the monohydrate Na_2CO_3,H_2O, also formed from the decahydrate at 35·4°. This is deposited as *crystal carbonate* from hot solutions on evaporation, and occurs native in the soda lakes of Egypt. There are two forms of $Na_2CO_3,7H_2O$, and other unstable hydrates.

Solutions containing less than 6·3 g. Na_2CO_3 per 100 g. water deposit ice on cooling (curve *AB*, Fig. 173). *B* is the eutectic point - 2·1°, where ice, solid

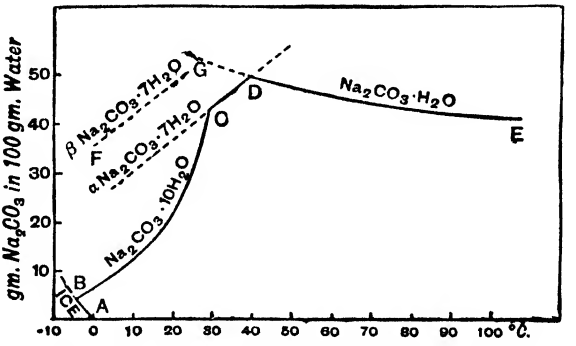


FIG. 173.—Solubility curves of sodium carbonate.

$Na_2CO_3,10H_2O$ and a solution containing 6·3 g. Na_2CO_3 per 100 g. water coexist in equilibrium with vapour ($C=2$; $P=4$; $\therefore F=0$). More concentrated solutions cannot exist in *stable* equilibrium with ice and $Na_2CO_3,10H_2O$, yet a solution of 18·46 g. Na_2CO_3 in 100 g. water may on cooling become unsaturated with respect to decahydrate and deposits ice at $-7·5°$. *BC* is the stable part of the solubility curve of decahydrate (the ordinary " solubility curve "). At *C* the solid decahydrate changes into a rhombic heptahydrate, α-$Na_2CO_3,7H_2O$ at

32·00°. *CD* is the stable solubility curve of this salt, which may be prolonged on both sides into metastable regions, shown dotted. At *D* the heptahydrate changes into monohydrate Na_2CO_3,H_2O at 35·37°, the solubility curve of which, with a prolongation into a metastable region shown dotted, is *DE*. Another heptahydrate β-$Na_2CO_3,7H_2O$, always metastable, separates along *FG*.

Sodium hydrogen carbonate $NaHCO_3$ (or *bicarbonate* $Na_2O,2CO_2,H_2O$) is formed in the ammonia-soda process but is converted into carbonate. A concentrated solution or moist crystals of sodium carbonate react with carbon dioxide to form a white crystalline powder of bicarbonate: $Na_2CO_3 + CO_2 + H_2O \rightleftharpoons 2NaHCO_3$, which is much less soluble:

	0°	10°	20°	30°	40°	50°
g. $NaHCO_3$/100 g. H_2O -	6·9	8·2	9·6	11·07	12·7	14·47

The precipitated salt is washed with a little cold water and dried in air. Any sodium chloride in the original carbonate is removed in this process, as it is more soluble, and on heating the bicarbonate at 250° the pure carbonate remains.

The pressures of $CO_2 + H_2O$ over bicarbonates of alkali metals (Caven and Sand, *J.C.S.*, 1911, **99**, 1359; 1914, **105**, 2752) are given by $\log p_{mm.} = A - B/T$, where T = abs. temp. The stability is smaller the larger the value of A.

	Na	K	Rb	Cs
A - -	11·8185	10·832	12·712	16·930
B - -	3340	3420	4300	6300

A solution of sodium bicarbonate is only slightly hydrolysed:

$$HCO_3' + H_2O \rightleftharpoons OH' + H_2CO_3,$$

and has an alkaline reaction which is much weaker than that of the carbonate. The salt can be recrystallised from hot water but on boiling the solution carbon dioxide is evolved. By prolonged boiling nearly all the bicarbonate is converted into carbonate, and if crude bicarbonate from the ammonia-soda process is boiled with water the ammonium salts are expelled as well. On recarbonating, almost pure sodium bicarbonate is precipitated and the commercial salt is made in this way.

On dissolving equimolecular amounts of sodium carbonate and bicarbonate in warm water and cooling to 35°, monoclinic crystals of **sodium sesquicarbonate** $Na_2CO_3,NaHCO_3,2H_2O$ deposit. This occurs in various localities as *trona* or *urao* and is formed by spontaneous evaporation of soda lakes, *e.g.* in Egypt. Large quantities occur in Searle's Lake in California, and Lake Magadi in East Africa. The artificial salt, known as *concentrated soda crystals*, is used in wool-washing. It is neither efflorescent nor deliquescent.

Potassium carbonate K_2CO_3 can be made from the chloride by a modification of the Leblanc process (p. 306). The bicarbonate $KHCO_3$ is too soluble to allow of its preparation by the analogue of the ammonia-soda process, so that the chloride is usually converted into carbonate by **Precht's process.**

A concentrated solution of potassium chloride is mixed with solid hydrated magnesium carbonate and carbon dioxide (limekiln gas) passed in, when a solid double salt is precipitated.

$$3(MgCO_3,3H_2O) + 2KCl\ aq. + CO_2 = 2(MgCO_3,KHCO_3,4H_2O) + MgCl_2\ aq.$$

The solid is stirred with water and magnesium oxide at 40° when potassium carbonate solution is formed and hydrated magnesium carbonate regenerated :

$$2(MgCO_3,KHCO_3,4H_2O) + MgO = 3(MgCO_3,3H_2O) + K_2CO_3.$$

Potassium carbonate is formed by strongly heating potassium salts of organic acids in air, and used to be made in this way from potassium hydrogen tartrate (*cream of tartar*), hence it was called *salt of tartar*. It is made in Russia, Central Europe, parts of the U.S.A. and Canada by extracting wood ashes with water, evaporating to dryness and calcining in iron pots. The *potash* so formed, when purified, is called *pearl ash*.

Potassium carbonate is a white powder, m.p. 900°; the m.p. is lowered (eutectic temp. 712°) when mixed with sodium carbonate (*fusion mixture*). It loses carbon dioxide when heated to redness in steam : $K_2CO_3 + H_2O = 2KOH + CO_2$. Unlike sodium carbonate it is deliquescent, as it is very soluble :

	0°	10°	25°	40°	60°	80°	135° (b.p. sat. sol.)
g. K_2CO_3/100 g. H_2O	105	—	113·5	117	127	140	205
g. $KHCO_3$/100 g. H_2O	22·1	27·7	36·1	45·3	60	—	—

The solution is strongly alkaline from hydrolysis :

$$CO_3'' + H_2O \rightleftharpoons HCO_3' + OH'.$$

There are two crystalline hydrates, $K_2CO_3,1\frac{1}{2}H_2O$, and below −6° $K_2CO_3,6H_2O$ (Hill and Miller, *J.A.C.S.*, 1927, **49**, 669).

Potassium hydrogen carbonate (*bicarbonate*) $KHCO_3$ is obtained by passing carbon dioxide over moist potassium carbonate, and drying on a porous plate over sulphuric acid in an atmosphere of carbon dioxide. It is much less soluble than the carbonate (see above) and is easily recrystallised from a warm solution by cooling. It is much more soluble than the sodium salt. It decomposes at 190° : $2KHCO_3 = K_2CO_3 + CO_2 + H_2O$.

Potassium sesquicarbonate $K_2CO_3,2KHCO_3,1\frac{1}{2}H_2O$ is much less stable than sodium sesquicarbonate (Hill, *J.A.C.S.*, 1930, **52**, 3817). A double sodium potassium carbonate $NaKCO_3,6H_2O$ has been described (Bain and Oliver, 1916).

Alkali Nitrates

Sodium nitrate $NaNO_3$ (*Chile saltpetre*) occurs in extensive deposits in the rainless districts between the ridges on the Tarapaca plateau and Antofogasti in Chile, where the richer part of the deposit is called *caliche*. This may contain 35–60 p.c. of $NaNO_3$ and some KNO_3, the rest being mostly NaCl. It is lixiviated with water and the nitrate crystallised (Donald, *Annals of Science*, 1936, **1**, 29, 193) ; it contains about 95 p.c. of $NaNO_3$ and usually some KNO_3 and is used as a fertiliser.

Sodium nitrate crystallises in rhombohedra resembling cubes, isomorphous with calcite, hence it is sometimes called "cubic nitre." It differs from potassium nitrate in being deliquescent, fuses at 316°, and at higher temperatures decomposes: $2NaNO_3 = 2NaNO_2 + O_2$.

The eutectic mixture of 55 p.c. KNO_3 and 45 p.c. $NaNO_3$ solidifies at 218° and is used as a heating bath, although it attacks glass rather strongly. A mixture of 54 p.c. KNO_3, 16 p.c. $NaNO_3$ and 30 p.c. $LiNO_3$ has a eutectic temperature of 120° and can be used in a pyrex beaker.

Potassium nitrate (*nitre* or *saltpetre*) is made in Bengal and Egypt from earth in which nitrogenous organic matter is oxidised to nitrate by nitrifying bacteria (p. 561), the earth being mixed with stable refuse, urine and calcium carbonate and exposed to air. The solution formed on lixiviation contains potassium and calcium nitrates; it is precipitated with potassium carbonate solution (from wood ashes) and the clear liquid evaporated and crystallised.

The solubilities of sodium and potassium nitrates are (g. in 100 g. H_2O):

	0°	10°	20°	40°	60°	80°	100°	120°
$NaNO_3$ -	73	80·5	88	104·9	124·6	148	175·5	209
KNO_3 -	13·3	20·9	31·6	63·9	110·0	169	246	394

Potassium nitrate is made from the cheaper sodium nitrate by adding this to a hot concentrated solution of potassium chloride. Sodium chloride deposits from the hot solution and on cooling the filtrate potassium nitrate crystallises, as it is much less soluble than sodium chloride at lower temperatures but much more soluble at higher temperatures (Fig. 36, p. 62; phase study by Cornec and Krombach, *Ann. Chim.*, 1929, **12**, 235). Potassium nitrate usually crystallises in large rhombic prisms, but on slow evaporation on a watch-glass the solution deposits rhombohedra isomorphous with sodium nitrate, and a second rhombohedral form is produced from the rhombic at 127°. Potassium nitrate melts at 336° and the fused salt is a powerful oxidising agent: sulphur, phosphorus and charcoal burn on it brilliantly. Potassium nitrate is used in pickling meat (to which it imparts a bright red colour, *e.g.* ham), in medicine, and especially in making gunpowder. The acid salts $KH(NO_3)_2$ and $KH_2(NO_3)_3$ are formed by crystallising from nitric acid (Groschuff, 1904).

Gunpowder is a finely powdered mixture of potassium nitrate, wood charcoal (carbonised at a relatively low temperature) and sulphur, approximately 75KNO_3, 14C, 10S and 1 moisture. The reaction on explosion is complex (Abel and Noble, 1875). The gaseous products are mainly CO_2, CO and N_2, the solid (including the dense smoke) K_2CO_3, K_2SO_4, and K_2S:

$$2KNO_3 + 3C + S = K_2S + N_2 + 3CO_2$$
$$2KNO_3 + 3C = K_2CO_3 + CO_2 + CO + N_2$$
$$4KNO_3 + 5C = 2K_2CO_3 + 2N_2 + 3CO_2$$
$$2KNO_3 + S + C = K_2SO_4 + N_2 + CO_2.$$

Alkali Phosphates

Ordinary sodium phosphate is **disodium hydrogen phosphate** (*secondary* sodium phosphate) crystallising in efflorescent monoclinic prisms $Na_2HPO_4,12H_2O$, m.p. 35°, soluble in water: g. Na_2HPO_4 in 100 g. H_2O: 10·26° 3·55, 25·15° 12·02, 40·29° 54·88, 99·77° 102·15. It is prepared by neutralising phosphoric acid with sodium hydroxide or carbonate (the end-point should be *faintly* alkaline) and evaporating. The effloresced salt contains $7H_2O$, there is a dihydrate, and on further exposure to dry air the anhydrous salt is finally formed (cf. Hammick, etc., *J.C.S.*, 1920, **117**, 1589). On heating it forms sodium pyrophosphate: $2Na_2HPO_4 = Na_4P_2O_7 + H_2O$.

Sodium dihydrogen phosphate (*primary* sodium phosphate, or acid sodium phosphate) is obtained by adding phosphoric acid to a solution of the secondary phosphate until it ceases to precipitate barium chloride and evaporating; rhombic crystals of NaH_2PO_4,H_2O separate on standing; there is also a dihydrate. At 100° it becomes anhydrous. The acid pyrophosphate is formed at 190°–200°: $2NaH_2PO_4 = Na_2H_2P_2O_7 + H_2O$, and above 300° the metaphosphate: $Na_2H_2P_2O_7 = 2NaPO_3 + H_2O$.

Trisodium phosphate (the *normal* or *tertiary* phosphate) is prepared by dissolving disodium hydrogen phosphate and a slight excess of sodium hydroxide in hot water, evaporating till a pellicle forms on the surface, and cooling. The tufts of crystals are recrystallised from twice the weight of hot water. The rhombohedral crystals $Na_3PO_4,12H_2O$ are neither efflorescent nor deliquescent. There are also hydrates with 10 and $7H_2O$. The crystalline salt (" tripsa ") is used in boiler-water softening: hydrolysis occurs in solution:

$$Na_3PO_4 + H_2O \rightleftharpoons Na_2HPO_4 + NaOH;$$

the calcium bicarbonate is precipitated as carbonate by the alkali, the calcium and magnesium chlorides and sulphates are precipitated as phosphates.

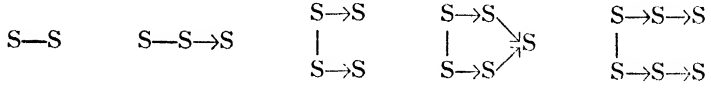
Microcosmic salt or **sodium ammonium hydrogen phosphate** $NaNH_4HPO_4,4H_2O$ is prepared by dissolving 6 g. of ammonium chloride and 36 g. of ordinary sodium phosphate in a little hot water, filtering from the sodium chloride in a hot-water funnel, and crystallising.

The common **potassium phosphate** is the primary salt KH_2PO_4, which forms tetragonal crystals; the secondary salt K_2HPO_4 (corresponding with common sodium phosphate) crystallises with great difficulty. The tertiary salt K_3PO_4 is prepared similarly to the sodium salt and is very soluble. The pyrophosphate $K_4P_2O_7$ and several forms of metaphosphate $(KPO_3)_n$ are known.

Alkali Sulphides

Alkali metal sulphides and polysulphides known from actual preparation and phase diagrams are as follows; when hydrates are known as well as anhydrous compounds the numbers of molecules of water of crystallisation are given in brackets (Pearson and Robinson, *J.C.S.*, 1931, 1983). Two of the polysulphides are most stable; one is always the disulphide M_2S_2 and the

other the tetrasulphide M_2S_4 in the case of lithium and sodium and the pentasulphide M_2S_5 in the case of potassium, rubidium and caesium. The bivalent polysulphide ions probably contain coordinate links :



Li_2S	Li_2S_2	—	Li_2S_4	—	—
Na_2S (9)	Na_2S_2 (2, 5, 6)	Na_2S_3 (3, 8)	Na_2S_4 (6, 8)	Na_2S_5 (6, 8)	—
K_2S (5)	K_2S_2 (3)	K_2S_3	K_2S_4 (2, 3)	K_2S_5 (1)	K_2S_6
Rb_2S (4)	Rb_2S_2 (3)	Rb_2S_3 (1)	Rb_2S_4 (2)	Rb_2S_5	Rb_2S_6
Cs_2S (4)	Cs_2S_2 (3)	Cs_2S_3 (1)	Cs_2S_4 (1)	Cs_2S_5	Cs_2S_6

Potassium and sodium burn in sulphur vapour forming mixtures of sulphides. On heating sulphur with excess of metal and heating the product at 200°–300° in vacuum the pure **monosulphides** K_2S and Na_2S remain. They form cubic crystals. Monosulphides are also formed (less pure) by passing hydrogen over the heated sulphates or by heating these with excess of carbon :

$$Na_2SO_4 + 4H_2 = Na_2S + 4H_2O$$
$$K_2SO_4 + 2C = K_2S + 2CO_2.$$

On passing the required amount of hydrogen sulphide into alkali hydroxide solution and evaporating colourless crystals of $Na_2S,9H_2O$ and $K_2S,5H_2O$ are formed. Sodium sulphide is made on the large scale by heating saltcake (Na_2SO_4) with powdered coal in a revolving furnace, extracting with water, and crystallising. The residual solution when mixed with sodium carbonate and treated with sulphur dioxide gives sodium thiosulphate :

$$2Na_2S + Na_2CO_3 + 4SO_2 = 3Na_2S_2O_3 + CO_2.$$

Sodium sulphide is used to remove hair from hides and to make sulphur dyes.

On saturating sodium or potassium hydroxide solution with hydrogen sulphide the sulphide first formed is converted into **hydrosulphide** and on evaporation $NaHS,3H_2O$ and $2KHS,H_2O$ crystallise. They lose water on heating. The anhydrous hydrosulphides are also formed by heating the metals in hydrogen sulphide, and pure by passing hydrogen sulphide into solutions of the ethoxides in anhydrous alcohol : $NaOC_2H_5 + H_2S = NaHS + C_2H_5OH$. They can be fused without decomposition.

Dark-coloured *liver of sulphur*, formed by fusing sulphur with potassium carbonate, contains polysulphides (p. 721).

By boiling alcoholic solutions of the hydrosulphides with sulphur, **potassium pentasulphide** K_2S_5 and **sodium tetrasulphide** Na_2S_4 are obtained. K_2S_5 forms bright orange-red crystals giving a deep orange solution which darkens on heating. Na_2S_4 forms dark yellow crystals giving a deep orange solution which

also darkens on heating. **Sodium disulphide** Na_2S_2, obtained by adding sodium to an alcoholic solution of Na_2S_4, forms bright yellow microscopic crystals giving a deep yellow solution which does not darken on heating.

Solutions of alkali sulphides and polysulphides are hydrolysed and react alkaline; the degree of hydrolysis decreases from the monosulphide to the pentasulphide and the hydrosulphides are much less hydrolysed. The percentage hydrolysis in $0{\cdot}1N$ solutions is:

NaHS	Na_2S	Na_2S_2	Na_2S_3	Na_2S_4	Na_2S_5
0·15	86·4	64·6	37·6	11·8	5·7

Alkali Sulphates

Normal sodium sulphate Na_2SO_4 occurs native (*e.g.* in Western Canada, the Western States of America, and in Russia) as *thenardite* and the hydrate $Na_2SO_4,10H_2O$ as *mirabilite*; *glauberite* is the double salt $CaSO_4,Na_2SO_4$, which is found in the Ebro valley. The anhydrous sulphate (m.p. 884°) is manufactured in what used to be the first stage in the Leblanc process (p. 306). Common salt is heated with concentrated sulphuric acid, when hydrogen chloride is evolved and can be absorbed in water, and sodium hydrogen sulphate is first formed. At a dull red heat this reacts with more salt to form sodium sulphate (*saltcake*):

$$NaCl + H_2SO_4 = NaHSO_4 + HCl$$
$$NaCl + NaHSO_4 = Na_2SO_4 + HCl.$$

Half a ton of coarse-grain salt is charged into the cast-iron pan *A* (Fig. 174) and an equal weight of sulphuric acid, s.g. 1·7, run on. Copious evolution of hydrochloric acid occurs, the gas being led off through *p*. When this slackens the pan is heated by flue gases admitted by dampers f_1 and f_2. When the first reaction is complete, the pasty mass is raked into the closed fire-brick box or *muffle B*, heated externally by flames from the gas producer *C*. The hydrochloric acid gas passes out through *d*. Saltcake is left in the muffle.

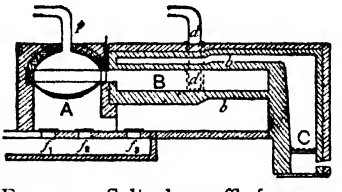


Fig. 174.—Saltcake muffle furnace.

In the **Hargreave's process** (1873) hot gas from pyrites burners, consisting of sulphur dioxide, oxygen and nitrogen, is passed with steam over porous pieces of common salt in large iron cylinders. Sodium sulphate is slowly formed, and hydrochloric acid gas evolved:

$$4NaCl + 2SO_2 + 2H_2O + O_2 = 2Na_2SO_4 + 4HCl.$$

The manufacture of saltcake has declined, partly because it has been replaced by soda ash (Na_2CO_3) in glass manufacture and partly because sodium sulphate is now recovered from residual liquors (containing NaCl and $MgSO_4$) of the Stassfurt potash industry: on cooling at −3° these deposit Glauber's salt ($Na_2SO_4,10H_2O$) which when dehydrated by heating yields very pure saltcake. Sodium sulphate is used in making kraft paper and in the textile industry.

The gas from saltcake furnaces, cooled by passing through iron pipes, is absorbed by water in stone towers packed with coke over which water is circulated : commercial hydrochloric acid (33 p.c.), called *spirit of salt*, is formed. Pure hydrochloric acid is now made synthetically (p. 778).

Glauber's salt $Na_2SO_4,10H_2O$ crystallises in large monoclinic prisms which effloresce in air to a powder of anhydrous salt. The crystals melt at 32·38° forming saturated solution and depositing anhydrous salt (the corresponding temperature for $Na_2SO_4,10D_2O$ is 34·48°). The solubility of sodium sulphate is a maximum at this temperature and the solubility curve consists of two parts meeting at a sharp angle at 32·38° (Fig. 175), the part below this temperature

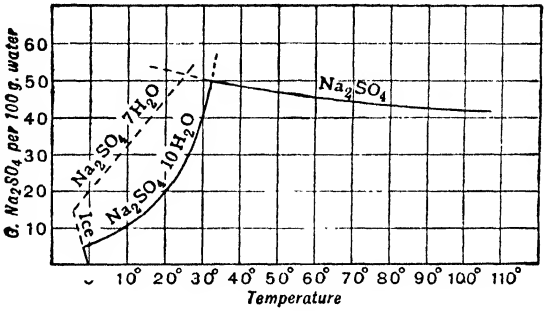


FIG. 175.—Solubility curves of sodium sulphate.

giving the solubilities of Glauber's salt and the part above that of anhydrous Na_2SO_4 (Gay-Lussac, *Ann. Chim.*, 1819, **11**, 296 ; Richards and Wells, *Z. phys. Chem.*, 1903, **43**, 471).

Sodium sulphate readily forms supersaturated solutions ; at 5° these deposit crystals of metastable $Na_2SO_4,7H_2O$, which become opaque in contact with Glauber's salt : $2Na_2SO_4,7H_2O = Na_2SO_4,10H_2O + Na_2SO_4 + 4H_2O$.

Sodium hydrogen sulphate (" bisulphate ") $NaHSO_4$, m.p. 185·7°, separates in large triclinic prisms from a solution of anhydrous sodium sulphate in warm concentrated sulphuric acid. It is formed as a by-product (*nitre cake*) in the manufacture of nitric acid (p. 567). The salts $NaHSO_4,H_2O$ and $NaHSO_4,Na_2SO_4$ are known (Faust and Esselmann, 1926). The acid sulphate is decomposed by alcohol (Dunnicliff, etc., *J.C.S.*, 1920, **117**, 649 ; 1923, **123**, 731) : $3NaHSO_4 \rightleftharpoons NaHSO_4,Na_2SO_4 + H_2SO_4$. (Dry $KHSO_4$ is not decomposed by alcohol.) The solution of $NaHSO_4$ is strongly acid ; on evaporation above 50° it gives crystals of $NaHSO_4$.

Sodium disulphate $Na_2S_2O_7$, m.p. 400·9°, is formed on gentle ignition of the acid sulphate : $2NaHSO_4 = Na_2S_2O_7 + H_2O$, by the action of sulphur trioxide on common salt : $2NaCl + 3SO_3 = Na_2S_2O_7 + SO_2Cl_2$, or (in the pure state) by the action of sulphur trioxide on the normal sulphate (Cambi and Bozza, *J.C.S.*, 1924, **126**, ii, 37) : $Na_2SO_4 + SO_3 = Na_2S_2O_7$. At a red heat it decomposes into sulphur trioxide and normal sulphate.

Normal **potassium sulphate** K_2SO_4 differs from sodium sulphate in crystallising anhydrous (rhombic prisms) and in its sparing solubility: 10·3 at 15°, 16·5 at 50°, 24·1 at 100°, in g. per 100 g. H_2O, the solubility increasing almost linearly with temperature (Fig. 36). It occurs as the double sulphates *glaserite* $NaK_3(SO_4)_2$ and *syngenite* $K_2Ca(SO_4)_2,H_2O$, and at Stassfurt as *picromerite* or *schönite* $K_2Mg(SO_4)_2,6H_2O$ and *kainite* $KMg(ClSO_4),3H_2O$, from a warm saturated solution of which schönite first crystallises. By digesting schönite with potassium chloride solution sparingly soluble potassium sulphate first crystallises:

$$K_2Mg(SO_4)_2 + 2KCl = 2K_2SO_4 + MgCl_2,$$

followed by carnallite $KMgCl_3,6H_2O$, from which potassium and magnesium chlorides can be prepared (p. 305).

Potassium sulphate is manufactured in small amounts by heating the chloride with sulphuric acid and as a by-product in the manufacture of potassium dichromate and permanganate. It is used in making potash alum and, as it has a high m.p. (1070°) and gives an infusible ash, as a fertiliser for tobacco: it improves the straw of wheat.

Potassium hydrogen sulphate, m.p. 219°, deposits in rhombic crystals from a warm solution of potassium sulphate in concentrated sulphuric acid (Rouelle, 1754). It is formed as a by-product in the laboratory preparation of nitric acid. It is readily soluble in water (51·4 g. in 100 g. H_2O at 20°) to form an acid solution, which on evaporation deposits K_2SO_4 and on cooling $K_3H(SO_4)_2$ and finally $KHSO_4$. The salts $K_5H_3(SO_4)_4$ and $K_8H_6(SO_4)_7$ are also known. On heating to dull redness potassium hydrogen sulphate forms **potassium disulphate** $K_2S_2O_7$, m.p. 414·2°: $2KHSO_4 = K_2S_2O_7 + H_2O$. At higher temperatures (it is more stable than $Na_2S_2O_7$) this evolves sulphur trioxide: $K_2S_2O_7 = K_2SO_4 + SO_3$, and fusion with $KHSO_4$ is used in making some minerals (*e.g.* chrome ironstone) soluble in analysis. Since loss of water from $KHSO_4$ on heating (even in vacuum) is incomplete, pure $K_2S_2O_7$ is best made by heating K_2SO_4 and sulphur trioxide.

Ammonium

The ammonium salts made from ammonia and acids contain the univalent **ammonium ion** NH_4^+, formed by addition of a proton to the lone pair of electrons on the nitrogen:

$$\begin{matrix} & H & \\ & \cdot\cdot & \\ H:N: & + & H^+ \\ & \cdot\cdot & \\ & H & \end{matrix} = \left[\begin{matrix} & H & \\ & \cdot\cdot & \\ H:N: & & H \\ & \cdot\cdot & \\ & H & \end{matrix}\right]^+ .$$

The four hydrogens are attached to the nitrogen by bonds directed towards the corners of a tetrahedron, the valency directions being like those of a carbon atom (p. 242). This was proved (Mills and Warren, *J.C.S.*, 1925, **127**, 2507) by the optical resolution of a spirane compound (Fig. 176), the tetrahedral arrangement of valencies being necessary to form a dissymmetric structure.

The analogy between ammonium and alkali metal compounds suggests that the neutral **ammonium radical** NH_4 might have metallic properties, and this is supported by the formation of an **ammonium amalgam** as a soft pasty mass by the action of sodium amalgam on a solution of ammonium chloride, or by electrolysis of the solution with a mercury cathode (Seebeck, 1808; Berzelius and Pontin, 1808; Davy, 1808). It decomposes at the ordinary temperature and forms hydrogen and ammonia in the ratio 1 : 2 by volume: $2NH_4 = H_2 + 2NH_3$.

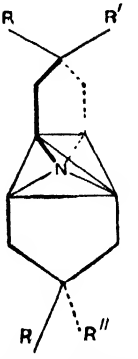


FIG. 176.—Tetrahedral structure of ammonium ion.

EXPT. 2.—Add some solid sodium amalgam (1–2 p.c.) to a cold saturated ammonium chloride solution. The amalgam swells up. Place a little of the ammonium amalgam in water: hydrogen is evolved and ammonia solution is formed.

Seely (1870) found that ammonium amalgam compressed in a tube under a piston obeys Boyle's law and hence concluded that it is only a mercury froth: this would not agree with its chemical properties. Although it does not reduce ferric chloride or copper solutions at ordinary temperature, it reduces solutions of copper, cadmium, zinc, and even barium salts at 0° (Coehn and Dannenberg, 1900). The voltage required to deposit sodium on a mercury cathode is similar to that required in the formation of ammonium amalgam (Le Blanc, 1890). An amalgam can be prepared by electrolysing a solution of tetramethyl-ammonium chloride $N(CH_3)_4Cl$ in absolute alcohol at 0° with a mercury cathode, and may contain the radical $N(CH_3)_4$, since it reduces copper and zinc salts in alcoholic solution (Palmaer, 1902).

The deep blue solutions of sodium or potassium in liquid ammonia have been regarded as metal ammoniums $NaNH_3$ and KNH_3 (Joannis, 1906), although the alkali metal can be filtered out by pressure (Ruff and Geisel, 1906). They seem to contain alkali metal ions, and free electrons combined with the solvent, and are conducting (Gibson and Phipps, *J.A.C.S.*, 1926, **48**, 312; Kraus, *J. Franklin Inst.*, 1931, **212**, 537; Taft, *J. Phys. Chem.*, 1930, **34**, 929).

According to Schlubach and Ballauf (*Ber.*, 1920, **53**, 1689; 1921, **54**, 2811, 2825) a colourless solution of free ammonium is formed by adding potassium to a solution of ammonium chloride in liquid ammonia at $-70°$. It decomposes, evolving hydrogen, at $-40°$.

AMMONIUM SALTS

Ammonium chloride NH_4Cl (*sal ammoniac*) is made: (i) by mixing dry hydrogen chloride diluted with hydrogen and nearly dry ammonia gas so that the temperature of reaction is 230°–310°: $HCl + NH_3 = NH_4Cl$; (ii) by the action of ammonium carbonate (or ammonia and carbon dioxide) on calcium chloride solution: $(NH_4)_2CO_3 + CaCl_2 = 2NH_4Cl + CaCO_3$, filtering and evaporating; (iii) by mixing equivalent amounts of ammonium sulphate and sodium chloride at 103° with enough water to form a saturated solution and crystallising at 30°: $(NH_4)_2SO_4 + 2NaCl = Na_2SO_4 + 2NH_4Cl$. A fibrous

form is made by sublimation from a mixture of ammonium sulphate and sodium chloride in a cast-iron pan with an iron dome having a small hole at the top: it forms tough irregular lumps often stained in yellow patches with ferric chloride. An imitation of the sublimed salt is made by process (i) or by strong compression of the powder; *voltoids* (used in Leclanché cells) are small compressed tablets. Ammonium chloride is also crystallised at low temperatures from the liquors from the bicarbonate filters in ammonia-soda works (p. 307) and dried in air.

Ammonium chloride was first made from ammonia and hydrochloric acid by Angelus Sala (1620). It crystallises in feathery aggregates of small octahedra so that the crystals look hexagonal or tetragonal ("crystal mimicry"). From a solution containing urea it crystallises in cubes. It exists in two forms with a transition point at 184·5°.

Ammonium chloride dissolves in water with lowering of temperature; the solubilities are:

	0°	20°	50°	100°	110°
g. in 100 g. H_2O	28·6	37·2	50·35	77·3	83·8

The solution is only slightly hydrolysed but loses ammonia and becomes acid on boiling (Smith, *J.S.C.I.*, 1911, **30**, 253). Ammonium chloride is *completely* dissociated on heating (Purcell and Lange, *J.C.S.*, 1929, 275): $NH_4Cl \rightleftharpoons NH_3 + HCl$.

According to Baker (*J.C.S.*, 1894, **65**, 611; 1898, **73**, 422; cf. Tramm, *Z. phys. Chem.*, 1923, **105**, 397; Smits, *ibid.*, 1935, **28B**, 31) the vapour density after drying over P_2O_5 corresponds with NH_4Cl and very dry ammonia and hydrogen chloride do not combine on mixing. Rodebush and Michalek (*J.A.C.S.*, 1929, **51**, 748), who used an impure salt which became yellow on heating, found that it dissociated even when dry but the rate of evaporation was much retarded.

The dissociation of ammonium chloride explains its use as a flux in soldering; the metal oxides are volatilised as chlorides and a clean metal surface is left: $CuO + 2HCl = CuCl_2 + H_2O$.

Ammonium fluoride NH_4F (used as an antiseptic in brewing), **bromide** NH_4Br and **iodide** NH_4I are obtained by neutralising the acids with ammonia. The **acid fluoride** NH_4HF_2 is formed on heating the fluoride: $2NH_4F = NH_4HF_2 + NH_3$. The bromide may be made by adding bromine to concentrated ammonia: $3Br_2 + 8NH_3 = N_2 + 6NH_4Br$, and the iodide by the action of ammonia solution and hydrogen peroxide on iodine: $I_2 + 2NH_3 + H_2O_2 = 2NH_4I + O_2$.

Ammonium chlorate NH_4ClO_3 is unstable and spontaneously explosive:

$$NH_4ClO_3 = NOCl + 2H_2O;$$

solutions may explode violently on evaporation. The **perchlorate** NH_4ClO_4 is more stable, but is endothermic and deflagrates with a yellow flame over 200°: $2NH_4ClO_4 = N_2 + Cl_2 + 2O_2 + 4H_2O$. The **iodate** decomposes on heating at 150°: $2NH_4IO_3 = N_2 + I_2 + O_2 + 4H_2O$.

Ammonium carbonates.—*Normal ammonium carbonate* $(NH_4)_2CO_3,H_2O$, first prepared by Dalton in 1813, is obtained (Divers, *J.C.S.*, 1870, **23**, 171) (i) by digesting commercial ammonium carbonate with concentrated ammonia for two hours at 12° and pressing the crystalline solid between filter papers with as little exposure to air as possible ; or (ii) more easily by passing ammonia gas at 15 cm. excess pressure into a mixture of 395 g. of commercial carbonate, 150 g. of water and 333 g. of 25 p.c. ammonia, warming at 40° till solution is complete, and then cooling to 10° (Terres, 1921).

Commercial ammonium carbonate (*sal volatile*) was made by subliming a mixture of chalk and ammonium chloride or sulphate in an iron retort, condensing in a well-cooled lead chamber and purifying by resublimation. It is now made by passing synthetic ammonia, carbon dioxide and some steam into a lead chamber. The product is a white translucent crystalline mass, smelling strongly of ammonia. It is a double compound of bicarbonate and carbamate, $NH_4HCO_3,NH_2{\cdot}CO{\cdot}ONH_4$. On exposure to air it leaves a white powder of **ammonium hydrogen carbonate** or *bicarbonate* NH_4HCO_3, which is made for use in baking powder. It can be crystallised, does not smell of ammonia at room temperature, but decomposes at 60° :

$$NH_4HCO_3 \rightleftharpoons NH_3 + CO_2 + H_2O.$$

The commercial carbonate digested at 30° with concentrated ammonia gives crystals of **ammonium sesquicarbonate** $2NH_4HCO_3,(NH_4)_2CO_3,H_2O$. On dissolving the commercial carbonate in ammonia solution the normal carbonate is formed :

$$NH_4HCO_3 + NH_3 = (NH_4)_2CO_3$$
$$NH_4O{\cdot}CO{\cdot}NH_2 + H_2O \rightleftharpoons NH_4O{\cdot}CO{\cdot}ONH_4.$$

Ammonium carbamate is formed as a white solid on mixing 2 vols. of ammonia gas and 1 vol. of carbon dioxide ; it dissociates on heating :

$$2NH_3 + CO_2 \rightleftharpoons NH_4O{\cdot}CO{\cdot}NH_2.$$

Under pressure at 135° in presence of a little water, **urea** is formed (Kolbe and Basaroff, 1868) and is now made technically by this process :

$$2NH_3 + CO_2 \rightleftharpoons NH_4O{\cdot}CO{\cdot}NH_2 \rightleftharpoons NH_2{\cdot}CO{\cdot}NH_2 + H_2O.$$

The system $NH_3 - CO_2 - H_2O$ has been studied by Terres (1928) and by Jänecke (1929–30), whose results are quite different.

Ammonium cyanide is manufactured by heating ammonia and carbon monoxide under pressure in presence of sodium and methyl alcohol, and passing the formamide produced with excess of ammonia over a bauxite catalyst at 300°–350° :

$$CO + 2NH_3 = H{\cdot}CO{\cdot}NH_2 + NH_3 = NH_4CN + H_2O.$$

Ammonium nitrate NH_4NO_3, discovered by Glauber, who called it *nitrum flammans* (as it deflagrates on sudden heating), is made on the large scale by passing ammonia gas into 60 p.c. nitric acid, when it remains fused.

Other processes which have been used are (i) the double decomposition of calcium nitrate and ammonium carbonate or sulphate; (ii) the double decomposition of sodium nitrate and ammonium sulphate; and (iii) using sodium nitrate instead of common salt in the ammonia-salt process:

$$NaNO_3 + NH_4HCO_3 \rightleftharpoons NH_4NO_3 + NaHCO_3.$$

A direct method of preparation has been described (p. 569).

Ammonium nitrate is deliquescent. It exists in five crystalline forms with definite transition temperatures (Early and Lowry, *J.C.S.*, 1919, **115**, 1387; 1922, **121**, 963; Hendricks, etc., *J.A.C.S.*, 1932, **54**, 2766):

$$\text{Tetragonal} \overset{-17^\circ}{\rightleftharpoons} (\text{Rhombic})_1 \overset{32{\cdot}1^\circ}{\rightleftharpoons} (\text{Rhombic})_2 \overset{84{\cdot}2^\circ}{\rightleftharpoons} \text{Rhombohedral} \overset{125{\cdot}2^\circ}{\rightleftharpoons} \text{Cubic} \overset{169{\cdot}6^\circ}{\rightleftharpoons} \text{Liquid}.$$

The melting point of the ordinary salt containing a little moisture is 165°. The transition at 84·2° occurs with expansion, which may break a glass vessel on cooling.

Ammonium nitrate is used in the preparation of nitrous oxide (p. 574). It deflagrates with a yellow flame above 250°: $2NH_4NO_3 = N_2 + 2NO + 4H_2O$, and at higher temperatures it detonates: $2NH_4NO_3 = 2N_2 + O_2 + 4H_2O$. Under reduced pressure it sublimes and at 11 mm. pressure it boils, the vapour being completely dissociated into HNO_3 and NH_3 (Rāy and Jānā, *J.C.S.*, 1913, **103**, 1565; Shah, *ibid.*, 1932, 731). It is a constituent of some explosives, *e.g.* a mixture (*amatol*) of 80 parts of ammonium nitrate and 20 parts of trinitrotoluene. A double salt $(NH_4)_2SO_4,2NH_4NO_3$ is *Leuna saltpetre*, a fertiliser; a large stock of it exploded at Oppau in 1921.

Ammonium nitrite NH_4NO_2 is obtained as an explosive deliquescent solid by passing the red gas $(NO + NO_2)$ from nitric acid and arsenious oxide over lumps of solid ammonium carbonate in a cooled tube, dissolving in alcohol, and precipitating with ether (Sörensen, *Z. anorg. Chem.*, 1894, **7**, 33). It is formed as a white powder by mixing the red gas with ammonia gas, although some ammonium nitrate is also produced, and it can be prepared by evaporating a concentrated solution of ammonium chloride and sodium nitrite in vacuum and subliming in vacuum (Neogi and Adhicary, *J.C.S.*, 1911, **99**, 116).

Ammonium sulphides.—The formation of colourless needles and plates of **ammonium hydrosulphide** NH_4HS by mixing equal volumes of ammonia and hydrogen sulphide was described by Bineau in 1838 and confirmed by Bloxam in 1893. Bineau in 1839 stated that a mixture of 2 vols. of ammonia with 1 vol. of hydrogen sulphide at −18° gave mica-like crystals of **ammonium monosulphide** $(NH_4)_2S$, but Bloxam found that these always contain ammonium hydrosulphide, and although he says he obtained the monosulphide by carefully adjusting the volumes of the reacting gases and their rates of flow, the product was probably contaminated with hydrosulphide (Thomas and Riding, *J.C.S.*, 1923, **123**, 1181). The pure hydrosulphide is precipitated in fine needles on passing dry ammonia and dry hydrogen sulphide alternately into dry ether. It dissociates rapidly and can be kept only in sealed vessels.

A solution of ammonium hydrosulphide NH_4HS, used as a reagent, is prepared by passing hydrogen sulphide into concentrated ammonia diluted with four volumes of water. (The normal sulphide does not seem to exist in solution.) The colourless freshly prepared solution oxidises in air and yellow polysulphides are formed. " Yellow ammonium sulphide ", used as a reagent for dissolving some metal sulphides, is made by digesting the hydrosulphide solution with flowers of sulphur: the main product seems to be **ammonium pentasulphide** $(NH_4)_2S_5$. A blood-red oil containing ammonium polysulphides was obtained by Beguin (1610) by distilling a dry mixture of ammonium chloride, quicklime and sulphur. On prolonged exposure to air, ammonium sulphide solution deposits sulphur and forms a colourless solution of **ammonium thiosulphate** $(NH_4)_2S_2O_3$.

Ammonium sulphate $(NH_4)_2SO_4$, described by Libavius (1597), is made by passing ammonia gas into fairly concentrated sulphuric acid (p. 550). In another process ammonia gas is absorbed in a suspension of anhydrite or calcined gypsum and carbon dioxide passed in:

$$CaSO_4 + 2NH_3 + CO_2 + H_2O = CaCO_3(pp.) + (NH_4)_2SO_4.$$

Ammonium sulphate forms large rhombic crystals isomorphous with potassium sulphate and very soluble in water:

	0°	20°	50°	100°
g. $(NH_4)_2SO_4$ in 100 g. H_2O -	70·0	75·5	77·8	101·7

Powdered ammonium sulphate on heating loses ammonia below 100° and at 300° is completely converted into fused **ammonium hydrogen sulphate**, m.p. 140°: $(NH_4)_2SO_4 = NH_4HSO_4 + NH_3$. At higher temperatures this decomposes with evolution of sulphur dioxide and nitrogen (Smith, *J.S.C.I.*, 1911, **30**, 253). The acid sulphate NH_4HSO_4 deposits in deliquescent rhombic crystals on cooling a solution of the normal sulphate in hot concentrated sulphuric acid. Alcohol decomposes it into the salt $(NH_4)_3H(SO_4)_2$ (Dunnicliff, *J.C.S.*, 1923, **123**, 476). **Ammonium sulphite** $(NH_4)_2SO_3$ is formed by passing sulphur dioxide into excess of concentrated ammonia solution and crystallises on cooling (Divers and Ogawa, *J.C.S.*, 1900, **77**, 335).

Lithium

Lithium is rare but widely distributed. It occurs in quantity only in a few rare minerals: *triphylite* $(Li,Na)_3PO_4$, $(Fe,Mn)_3(PO_4)_2$ with 1·6–3·7 p.c. Li, *petalite* $LiAl(Si_2O_5)_2$ with 2·7–3·7 p.c. Li, *lepidolite* or *lithium mica* $(Li,Na,K)_3Al_2(SiO_3)_3(F,OH)_2$, *amblygonite* $Li(F,OH)AlPO_4$ with 2·4–3 p.c. Li, and *spodumene* $LiAl(SiO_3)_2$ with 3·8–5·6 p.c. Li. The element was discovered in petalite and spodumene by Arfvedson in 1817 and named by Berzelius, from the Greek *lithos*, a stone. It also occurs in some mineral springs, *e.g.* in Baden and at Redruth in Cornwall, in some radioactive minerals *e.g.* carnotite, in the sea, the soil, milk, blood, and plants, especially tobacco. Traces of lithium occur in most kinds of glass.

Metallic lithium, the lightest metal known (density 0·53 at 20°), was isolated by Davy in 1818 by electrolysis of the oxide and by Bunsen and Matthiessen

in 1855 by electrolysis of the fused chloride. Lithium may also be obtained by the electrolysis of lithium bromide containing 13 per cent. of lithium chloride. It is silver-white, harder than sodium, tarnishing in air although less readily than other alkali-metals, and decomposing water with evolution of hydrogen. It does not fuse on water like sodium and potassium, since its melting point (180°) is higher. Lithium readily combines with nitrogen, slowly even at room temperature, to form the **nitride** Li_3N. (It is the only alkali metal which combines directly with nitrogen.)

Lithium-lead **alloy** is used as a bearing metal and for cable sheaths; a zinc-aluminium-lithium **alloy** (0·1 p.c. Li) has properties resembling those of mild steel. Lithium improves the tensile strength and corrosion resistance of aluminium alloys; the alloy with calcium is used in purifying high-conductivity copper.

Lithium salts are extracted from the minerals in various ways. In one, the finely powdered mineral is digested with concentrated sulphuric or hydrochloric acid, which is evaporated to render silica insoluble. The residue is taken up with water and the solution filtered, the requisite amount of sodium carbonate is added to precipitate iron, aluminium, magnesium, etc., and the filtrate is concentrated by evaporation. Excess of sodium carbonate is added, when **lithium carbonate** Li_2CO_3 is precipitated, as it differs from other alkali carbonates and resembles the alkaline earth carbonates in being sparingly soluble. Another process is to fuse the mineral with barium carbonate and sulphate, extract with water, precipitate the filtrate with barium chloride and evaporate to dryness. The residue contains sodium, potassium and lithium chlorides, and is digested with a mixture of absolute alcohol and ether, in which lithium chloride alone is soluble.

Lithium chloride LiCl, m.p. 606°, is one of the most deliquescent substances known: it forms compounds with water and with ammonia. **Lithium fluoride** LiF is sparingly soluble (cf. CaF_2).

Lithium burns in oxygen with a white flame when heated above its melting point, forming the white **monoxide** (*lithia*) Li_2O, which dissolves *slowly* in water with only moderate rise of temperature, forming **lithium hydroxide** LiOH. This is made by decomposing a solution of lithium sulphate Li_2SO_4 with baryta water. It crystallises as $LiOH,H_2O$ and is a strong base. On heating the crystals in hydrogen below 140° a white porous mass of LiOH remains, and at 780° the oxide Li_2O is formed. A **peroxide** Li_2O_2 is formed by drying over P_2O_5 the precipitate $Li_2O_2,H_2O_2,3H_2O$ obtained by adding hydrogen peroxide and alcohol to a solution of the hydroxide.

Lithium carbonate Li_2CO_3 and **lithium phosphate** Li_3PO_4 are sparingly soluble and are precipitated by the sodium salts: the carbonate dissolves in water containing carbon dioxide, forming *lithia water*, which may contain $LiHCO_3$. The carbonate decomposes completely into the oxide and carbon dioxide on heating in a stream of hydrogen at 780°: $Li_2CO_3 = Li_2O + CO_2$. In these reactions lithium resembles the alkaline earths. **Lithium sulphate** Li_2SO_4,H_2O, however, is easily soluble.

Lithium nitrate $LiNO_3,3H_2O$ (cf. Donnan and Burt, *J.C.S.*, 1903, **83**, 335) is very deliquescent and soluble in alcohol.

Lithium salts are used in making some glasses and glazes and the citrate and salicylate in medicine as a remedy for gout, since lithium urate is fairly soluble (1 pt. in 368 pts. H_2O at 20°).

Lithium salts give a crimson flame coloration rather like that of strontium. It is resolved by the spectroscope into a very weak yellow line (6104 A.) and a brilliant crimson line (6708 A.). Lithium is separated from potassium by the solubility of its chloroplatinate Li_2PtCl_6, and from sodium by the solubility of its chloride in a mixture of absolute alcohol and ether or in pyridine, in which sodium chloride is insoluble.

Rubidium and **caesium** are very rare. They occur in small quantities in some mineral waters and rubidium salts are absorbed by plants and remain in the ash. Lepidolite may contain 2·6 p.c. of Rb and carnallite 0·035 p.c. of RbCl, which collects in the mother-liquor of potassium chloride (p. 305) and may be extracted from it. Traces of rubidium are widely distributed, but caesium is very rare; it is present in the rare mineral *pollux* (or *pollucite*), a hydrated caesium aluminosilicate which is found only on the island of Elba and (less rich) in Maine, U.S.A. Caesium chloride occurs in the water of Wheal Clifford Spring in Cornwall.

Rubidium and caesium are difficult to separate; they may be separated from the other alkali metals and from each other by the different solubilities of the chloroplatinates (the sodium and lithium salts are soluble) and alums, the solubilities (g./100 g. H_2O) at 20° being:

	K	Rb	Cs
Alums:	13·5	2·27	0·619
M_2PtCl_6:	1·12	0·141	0·070

Caesium may be separated as the characteristic *Godefroy's salt* $Cs_3Sb_2Cl_9$, precipitated by a solution of antimony trichloride in hydrochloric acid, which is decomposed by ammonia to give caesium chloride.

Metallic caesium (first obtained by Setterberg in 1882) is best prepared by distilling the chloride with a large excess of calcium in vacuum in a nickel tube and condensing the vapour in a glass receiver (Kennedy, *Chem. Reviews*, 1938, **23**, 157); it is used in photoelectric cells, in which a very thin film of the metal is deposited on a very thin film of caesium oxide supported on silver. Both rubidium and (especially) caesium are very soft at room temperature and have a silver-white lustre; caesium oxide Cs_2O is peculiar in being red.

CHAPTER XIII

COPPER, SILVER AND GOLD

THE general properties of the odd series elements of Group I are as follows:

	Copper	Silver	Gold
Atomic number	29	47	79
Electron configuration	2·8·18·1	2·8·18·18·1	2·8·18·32·18·1
Density at 15°	8·96	10·47	19·3
Atomic volume	7·10	10·3	10·2
Melting point	1083·0°	960·5°	1063·0°
Boiling point	2310°	1955°	2610°
Colour of vapour	green	blue	yellowish-green

The rather small atomic volumes result from the high nuclear charges drawing electron shells near them towards the nucleus.

The varying valency of copper, silver and gold is due to the fact that these are *transitional elements* (p. 261), and the *inner* group of 18 electrons can be drawn upon for one or two valency electrons. The bivalent copper and silver ions have 17 electrons in the incomplete outer group, and as an odd electron is present the ions are coloured and paramagnetic (p. 271). The tervalent gold compounds are probably always covalent.

The cupric compounds show many analogies with those of Group II metals and also to other metals in the bivalent state. Cupric sulphate $CuSO_4$ has a resemblance to the sulphates of magnesium and zinc and those of bivalent iron, nickel, cobalt and manganese, and crystal hydrates containing the same number of molecules of water are isomorphous. The double sulphates with alkali metals are analogous in composition and crystal form.

There are distinct resemblances in the triad Pd,Ag,Cd, and to a less degree in Pt,Au,Hg, although copper and mercury are more closely related and silver shows some analogies with lead and mercurous mercury, *e.g.* in the properties of the chlorides.

Copper is much less easily oxidised than the alkali metals, and silver and gold are " noble " metals, not oxidised by heating in oxygen (although fused silver seems to form an oxide which dissolves in the metal; this loses oxygen and " spits " on solidification). Silver and gold compounds are also very easily reduced to the metals, and their oxides are easily decomposed by heat, whereas the oxides of copper are distinctly stable. This is connected with the heats of formation (p. 295). Copper, silver and gold are near the end of the electrochemical series (p. 97), and are easily displaced by other metals such as zinc and iron (even mercury in the case of silver) from solutions of their salts, silver and gold being precipitated by copper, which has a much smaller positive electrode potential.

Silver is predominantly univalent and its halogen compounds resemble the corresponding cuprous compounds. Silver oxide is a much stronger base

sulphate solution acidified with sulphuric acid and made the anodes. The cathodes are thin sheets of pure copper previously deposited by electrolysis on copper plates covered with a layer of graphite and oil. The copper anode dissolves and copper ions are deposited on the cathode as pure copper. Iron, nickel, cobalt and zinc dissolve as sulphates along with any arsenic ; gold, silver and any platinum metals, together with some impurities (selenium, tellurium, lead, bismuth, tin and antimony) deposit as *anode slime*, which is collected to recover the precious metals. A ton of American copper contains about 110 oz. of silver and ½ oz. of gold. The electrolytic copper is 99·96–99·99 p.c. pure.

A similar process is **electrotyping**, used in reproducing statues and other works of art. The copper may be deposited on plaster casts covered with graphite and the shell stripped off. In the same way an impression of printers' type is taken on a plastic material, the latter covered with powdered graphite, and a thin deposit of copper formed by electrolysis. Copper may be deposited on iron by dipping this in a solution of copper cyanide in potassium cyanide, when a thin *adherent* film of copper is deposited (a spongy deposit is produced from copper sulphate) and this is thickened by electrolysis in a solution of copper sulphate. Iron rollers are in this way covered with copper for use in calico-printing.

Copper is used for the driving-band of steel projectiles, a copper band recessed into a groove in the base of the shell and projecting slightly above the surface so as to squeeze into the spiral rifling of the gun-barrel and cause the projectile to rotate.

Properties of copper.—A clean copper surface is light red, but the colour seen by selective reflection in a V-shaped piece of copper foil cleaned with nitric acid is deep rose-red. The complementary colour, green, is transmitted through thin leaves of copper or emitted by molten copper. In solution in mercury or fused tin copper is monatomic.

Pure copper is very malleable and ductile : it can be rolled into sheets, hammered into thin leaves, drawn into wire, and " spun " on a lathe to form seamless vessels. Just below the m.p. it becomes brittle. The density is 8·9559 at 15°. The m.p. in vacuum is 1083°, in air (when some cuprous oxide dissolves) 1063°. The b.p. is 2310°, and it can be distilled in a high vacuum. The spongy or fused metal occludes gases, and when fused copper containing cuprous oxide solidifies the oxygen is liberated and the metal " spits " like silver (p. 345).

On striking an arc under water between copper wires a colloidal solution is obtained, but this probably contains oxide. By dialysing a solution of copper sulphate, sodium hydroxide and sodium lysalbate or protalbate, and then reducing by warming with hydrazine, a dark red colloidal solution of copper is produced. If only partly reduced a yellowish-red colloidal solution of cuprous oxide is obtained. A copper mirror is formed on heating in hot water a clean test-tube containing an ammoniacal solution of copper acetate decolorised by hydrazine solution (p. 558).

Pure copper powder is produced by dissolving zinc in a slightly acidified solution of copper sulphate, washing the precipitate with hot water and alcohol, and removing the small quantity of occluded hydrogen by heating in a vacuum.

Magnesium precipitates copper solutions incompletely, some cuprous oxide and basic salt being precipitated and hydrogen evolved :

$$2Mg + 2CuSO_4 + H_2O = 2MgSO_4 + Cu_2O + H_2$$

(Commaille, *Compt. rend.*, 1866, **63**, 556 ; Clowes, *Proc. C.S.*, 1897, **13**, 221 ; Caven, *J.S.C.I.*, 1900, **19**, 18).

In ordinary air copper rapidly acquires a brown protective tarnish of oxide or sulphide. (It is attacked by hydrogen sulphide only in presence of oxygen, cf. Ag, p. 345). Exposure to town air forms a green patina of basic sulphate $[Cu\{Cu(OH)_2\}]SO_4$, which slowly forms $[Cu\{Cu(OH)_2\}_3]SO_4$; in sea air basic chloride $[Cu\{Cu(OH)_2\}_3]Cl_2$ is formed (Vernon, *J.C.S.*, 1934, 1853). On heating in air the metal easily oxidises to scales, black (CuO) outside and red (Cu_2O) in contact with the copper : on prolonged heating in air cupric oxide CuO is formed. Copper wire burns with a brilliant green flame in the oxy-hydrogen blowpipe flame.

Alloys of copper are of technical importance. *Brass* (copper + zinc) and *bronze* (copper + tin) are made by melting the copper and adding the other metal. The f.p. diagrams show that some compounds, and solid solution phases, are formed (p. 250). Copper with 0·3–0·5 p.c. of arsenic is stronger at high temperatures than pure copper. Bronze is much less corroded by sea water than copper or brass.

Casting bronze usually contains some zinc and lead as well as tin. Bronze for machinery contains 80–90 Cu, 5–18 Sn and 2–10 Zn ; *gun metal* is 9 Cu and 1 Sn, *speculum metal* 2 Cu and 1 Sn, *bell metal* 4–5 Cu and 1 Sn, modern bronze coin is 95 Cu, 4 Sn and 1 Zn.

The best *brass* is 4 Cu and 1 Zn, common brass contains 22–30 p.c. of Zn, but metal with 35–40 p.c. Zn can still be worked. *Silicon bronze* is used for telegraph wires ; *phosphor bronze* (containing 5–15 p.c. Sn and 0·25–2·5 p.c. P) is hard, elastic, and tough ; *beryllium bronzes* (2·5–2·75 p.c. Be) when heat-treated are as hard as steel ; *delta metal* (55 Cu, 41 Zn, 4 Fe) is used for bearings, valves and ships' propellers, and can be forged and rolled as well as cast ; *muntz metal* is 3 Cu and 2 Zn, used for sheathing wooden ships ; *Dutch metal* is similar to brass, *Monel metal* is 7 Cu and 3 Ni.

Cupric Compounds

Cupric oxide CuO or *black oxide of copper* is formed by the prolonged heating of copper turnings in air or oxygen, but the product may contain some cuprous oxide ; also by heating copper nitrate : $2Cu(NO_3)_2 = 2CuO + 4NO_2 + O_2$, but the product contains occluded oxygen and nitrogen. A purer oxide is obtained by heating the basic carbonate (Richards, 1898). It is stable to about 800°, but at higher temperatures evolves oxygen and forms some cuprous oxide. It does not melt without decomposition below 1233°. Copper and cuprous oxide form a broken series of solid solutions on solidification but Cu_2O and CuO do not form solid solutions (Smyth and Roberts, *J.A.C.S.*, 1920, **42**, 2582). Cupric oxide is readily reduced to copper by hydrogen, carbon or organic substances below redness. It dissolves in the borax bead, colouring it blue.

If a little tin oxide or stannous chloride is added, the cupric oxide is reduced to cuprous oxide, which forms a red bead (Bancroft and Nugent, *J. Phys. Chem.*, 1929, **33**, 729). Cupric and cuprous oxides are used to give blue and red colours to glass.

Cupric oxide dissolves in dilute acids to form blue solutions of cupric salts : $CuO + H_2SO_4 = CuSO_4 + H_2O$. Concentrated hydrochloric acid gives a yellow solution of cupric chloride $CuCl_2$.

Cupric hydroxide $Cu(OH)_2$ is formed as a pale blue gelatinous precipitate on mixing solutions of alkali hydroxide and a cupric salt in equivalent amounts or with the hydroxide in excess. It is insoluble in excess of dilute sodium or potassium hydroxide but forms a blue solution with ammonia. With excess of cupric salt a basic salt, *e.g.* $CuSO_4,3Cu(OH)_2$, is precipitated, as Berthollet knew (see p. 4).

Crystalline $Cu(OH)_2$ is formed by adding ammonia to boiling copper sulphate solution till the green precipitate turns blue, washing, and digesting with fairly concentrated sodium hydroxide solution at 20°–40° (Habermann, 1906).

On boiling the pale blue hydroxide with water, especially in presence of alkali, it forms a granular black solid, easily filtered, and usually formulated as $4CuO,H_2O$. At a red heat this forms CuO.

According to Champetier and Thuau (1932) and Weiser, Milligan and Cook (*J.A.C.S.*, 1942, **64**, 503), $Cu(OH)_2$ is the only hydrate of CuO ; a black colour is due to CuO spontaneously formed by dehydration of the gel, this being accelerated by contact with dilute alkali.

On adding a little copper salt solution to excess of concentrated alkali hydroxide a deep blue solution is formed which probably contains colloidal cupric hydroxide, although a **cuprate**, *e.g.* K_2CuO_2, may be present (Creighton, *J.A.C.S.*, 1923, **45**, 1237). Solid cuprates, *e.g.* $Na_2[Cu(OH)_4]$ and $Ba_2[Cu(OH)_6]$ are described (Scholder, 1933).

Cupric hydroxide readily dissolves in ammonia, forming a deep blue solution known as *Schweizer's reagent*. It probably contains $Cu(OH)_2(NH_3)_2$ and with excess of ammonia $Cu(OH)_2(NH_3)_4$. It dissolves cellulose (filter paper, cotton wool), and if the solution is squirted into dilute acid a thread of amorphous cellulose is formed which is one variety of artificial silk. The solution may also be applied to canvas to form a water-tight coating of amorphous cellulose (*Willesden canvas*) : some method of preserving cellulose by impregnation with copper was known in ancient Egypt.

A red **copper sesquioxide** Cu_2O_3, probably containing tervalent copper, is formed by the action of potassium persulphate on a suspension of cupric hydroxide in baryta water (Aldridge and Applebey, *J.C.S.*, 1922, **121**, 238) or by electrolytic oxidation of copper in very concentrated sodium hydroxide (Scagliarini and Torelli, *Gazz.*, 1921, **51**, ii, 225 ; Vrtis, *Rec. Trav. Chim.*, 1925, **44**, 425), and it appears to form **percuprates**, *e.g.* $BaCu_2O_4$. Hydrogen peroxide converts cupric hydroxide, or a solution of cupric hydroxide in potassium hydroxide, or sodium cupric **carbonate**, into yellowish-brown hydrated **copper dioxide** CuO_2,H_2O or $O=Cu(OH)_2$

containing quadrivalent copper. An alternative formulation is CuO,H_2O_2, as it forms hydrogen peroxide with acids.

Cupric fluoride CuF_2 is a white powder formed by the action of fluorine on copper powder or by heating the blue crystalline hydrate $CuF_2,2H_2O$ (formed by evaporating a solution of CuO in hydrofluoric acid) in hydrogen fluoride gas below 500°.

Cupric chloride $CuCl_2$ is obtained anhydrous as a dark brown mass by burning copper in excess of chlorine, or by heating the hydrate $CuCl_2,2H_2O$ in hydrogen chloride gas at 150°. It is formed as a yellow powder by adding concentrated sulphuric acid slowly to a concentrated solution of cupric chloride. When strongly heated it loses chlorine and leaves cuprous chloride. A crystalline hydrate $CuCl_2,2H_2O$ is formed in emerald-green crystals by dissolving cupric oxide in concentrated hydrochloric acid and evaporating. When quite free from adhering saturated solution (yellow) the crystals are blue. Concentrated solutions are yellowish-green and on adding concentrated hydrochloric acid become yellow. This is usually said to be due to reversal of ionisation: $CuCl_2 + 4H_2O \rightleftharpoons Cu(H_2O)_4^{\cdot\cdot} + 2Cl'$, the colour of the undissociated salt, *e.g.* in some organic solvents, being yellow. A very dilute solution shows the pure blue colour of the hydrated cupric ion; the green solutions probably contain a mixture of the blue ion and the yellow un-ionised salt, although complex anions may be present (Donnan and Bassett, *J.C.S.*, 1902, **81**, 939): $2CuCl_2 \rightleftharpoons Cu^{\cdot\cdot} + CuCl_4''$. The blue solution in pyridine is a non-conductor and perhaps contains $[CuCl_2py_2]$. The colour change from yellow to blue on dilution may arise from the succession $[CuCl_4]''$, $[CuCl_3(H_2O)]'$, $[CuCl_2(H_2O)_2]$, $[CuCl(H_2O)_3]^{\cdot}$, and $[Cu(H_2O)_4]^{\cdot\cdot}$ (Kohlschütter, 1904). Cupric chloride is very deliquescent and is soluble in methyl and ethyl alcohols, from which green crystals $[Cu(ROH)_2Cl_2]$ can be obtained. The alcoholic solution burns with a fine green flame.

On saturating a concentrated solution of cupric chloride with hydrogen chloride and cooling dark red needles of one of the complex acids $HCuCl_3,3H_2O$, $H_2CuCl_4,5H_2O$ and H_3CuCl_5 are obtained (Engel, 1888; Sabatier, 1888; Naumann, 1894), various salts of which are known, $KCuCl_3$ (red), $K_2CuCl_4,2H_2O$ (green), Cs_2CuCl_4 (yellow), etc. $CuCl_2$ forms ammines with 6, $\frac{10}{3}$, 4 and 2 NH_3; $Cu(NH_3)_4Cl_2,2H_2O$ crystallises on cooling a hot solution of $CuCl_2$ saturated with ammonia gas.

Cupric oxychloride $CuCl_2,3Cu(OH)_2$ or $[Cu\{Cu(OH)_2\}_3]Cl_2$ is formed as a pale blue precipitate when sodium hydroxide is added to an excess of cupric chloride solution. It occurs in Atacama, Peru, Bolivia, etc., in the form of a crystalline green sand called *atacamite*, and is formed by the action of sea water on copper pyrites on the south coast of Chile and in Adelaide, Australia. The oxychloride is made as a pigment (*Brunswick green*) by boiling copper sulphate solution with a small quantity of bleaching powder.

Cupric bromide $CuBr_2$ is formed in black crystals by evaporating a solution of the oxide in hydrobromic acid in vacuum over quicklime. In water it shows the same colour sequence on dilution as the chloride. The solution in pyridine

is blue, in acetone green, in concentrated hydrobromic acid purple, and crystalline $HCuBr_3,2H_2O$ and corresponding salts are known. The green hydrate $CuBr_2,H_2O$ is not easily obtained.

Cupric iodide CuI_2 is not stable (see p. 339) but forms stable crystalline coordination compounds with ammonia: $[Cu(NH_3)_4]I_2,H_2O$ (blue tetrahedra; Berthemot, 1830) and the anhydrous compound (King, *J.C.S.*, 1930, 2307), and ethylenediamine $[Cu\ en_2]I_2$,1 and $2H_2O$ (Morgan and Burstall, *J.C.S.*, 1926, 2018).

Cupric carbonates.—Only *basic* cupric carbonates are known, the most important being the minerals *chessylite* or *azurite*: $2CuCO_3,Cu(OH)_2$ or $Cu_3(OH)_2(CO_3)_2$ (deep blue), and *malachite* $CuCO_3,Cu(OH)_2$ or $Cu_2(OH)_2CO_3$. The hydroxy-carbonate structures are shown by X-ray analysis (Brasseur, 1931).

The green patina formed on copper exposed to air is not the basic carbonate but nearly always the basic sulphate (p. 330).

The pale blue precipitate of basic carbonate formed on adding sodium carbonate solution to a cupric salt solution has the composition of azurite (Dunnicliff and Lal, *J.C.S.*, 1918, **118**, 718). Blue crystalline **sodium cupricarbonate** $Na_2[Cu(CO_3)_2],3H_2O$ is formed by warming the precipitated basic carbonate with sodium carbonate and bicarbonate solution (Reynolds, *J.C.S.*, 1898, **73**, 262; Applebey and Lane, *ibid.*, 1918, **113**, 609). Cupric carbonate is stable in coordination compounds with ammonia $[Cu(NH_3)_2]CO_3$ (Favre, 1844) and ethylenediamine $[Cu\ en_2]CO_3,2H_2O$ (Morgan and Burstall, *J.C.S.*, 1927, 1259).

Cupric cyanide is very unstable (p. 340), but forms a coordination compound with pyridine $[Cu^{II}\ py_2](CN)_2$ (Varet, 1891). With ethylenediamine compounds containing univalent copper in the anion,

$$[Cu^{II}\ en_2]\ [Cu^{I}(CN)_2]_2,H_2O \text{ and } [Cu^{II}\ en_2]\ [Cu^{I}_2(CN)_3]_2$$

are formed (Morgan and Burstall, *J.C.S.*, 1926, 2018). **Cupric thiocyanate** $Cu(CNS)_2$ is formed as a black precipitate, soluble in pyridine (Partington and Skeen, *T. Faraday Soc.*, 1936, **32**, 975); it forms stable compounds with pyridine $[Cu\ py_2](CNS)_2$ and $[Cu\ py_4](CNS)_2$ (Litterscheid, 1902) and ethylenediamine $[Cu\ en_2](CNS)_2$ (Morgan and Burstall, 1927, also $[Cu\ en_2](CNSe)_2$).

Grey **copper silicide** Cu_2Si is formed from the elements in the electric furnace; copper containing 1–2 p.c. of silicon is hard but has a good electrical conductivity, and is used for telegraph wires and sliding contacts. **Copper silicates** occur as the minerals *dioptase* $CuSiO_3,H_2O$ and *chrysocolla* $CuSiO_3,2H_2O$ (the ancient chrysocolla was probably malachite).

Cupric nitrate is formed in blue deliquescent prismatic crystals on evaporating a solution of copper, copper oxide or basic carbonate in dilute nitric acid. At 24·5° $Cu(NO_3)_2,6H_2O$ and at −20° $Cu(NO_3)_2,9H_2O$ separate. On heating, the crystals lose water and nitric acid and form the basic salt $Cu(NO_3)_2$, $3Cu(OH)_2$, also precipitated from solution by ammonia. Copper nitrate is a powerful oxidising agent; if a few crystals are moistened, wrapped in tinfoil and

pressed, sparks are emitted. The anhydrous salt is formed as a white powder by the action of a solution of nitrogen pentoxide in concentrated nitric acid on the hydrate, and drying over CaO and P_2O_5 (Guntz and Martin, 1909).

Cupric nitrite is known only as a green solution (p. 566) and in complex and coordination compounds,

$$K_3[Cu(NO_2)_5],\ K_2Ca[Cu(NO_2)_6],\ [Cu(NH_3)_4(H_2O)_2](NO_2)_2$$

(Peligot, 1861), $[Cu(NH_3)_4](NO_2)_2$ (Pudschies, 1904) and $[Cu\ en_2](NO_2)_2$ (Morgan and Burstall, *J.C.S.*, 1927, 1259).

The black powder formed on boiling white phosphorus with cupric sulphate solution is usually described as **cupric phosphide** Cu_3P_2 and the precipitate with phosphine as Cu_5P_2,H_2O, but the freezing-point diagram shows that the only stable compound is **cuprous phosphide** Cu_3P (Haraldsen, 1939), although CuP_2 can exist in equilibrium with copper and phosphorus. The black substance may be Cu_3P: $3P + 3CuSO_4 + 6H_2O = Cu_3P + 2H_3PO_3 + 3H_2SO_4$.

Cupric phosphate $Cu_3(PO_4)_2,3H_2O$ is obtained as a blue crystalline precipitate on dissolving the basic carbonate in dilute phosphoric acid and heating at 70°; on boiling with water it forms $Cu_3(PO_4)_2,Cu(OH)_2$ (Caven and Hill, *J.S.C.I.*, 1897, **16**, 29). **Cupric hypophosphite** (cf. p. 337) (Engel, 1899) and the coordination compound with ethylenediamine $[Cu\ en_2]\ (H_2PO_2)_2$ (Morgan and Burstall, *J.C.S.*, 1927, 1259) are known.

Cupric sulphide CuS is formed as a black solid by heating copper powder and excess of flowers of sulphur below 440°, by the action of a solution of sulphur in carbon disulphide on copper powder, and impure, containing cuprous sulphide and sulphur (Abel, 1901), by precipitating an acidified cupric salt solution with hydrogen sulphide, or a solution of copper sulphate with sodium sulphide. When moist it rapidly oxidises to sulphate in air. It is less stable than cuprous sulphide and decomposes into this and sulphur when moderately heated alone or in hydrogen: $2CuS = Cu_2S + S$. It is slightly soluble in yellow ammonium sulphide and from the hot solution red crystals of NH_4CuS_4 are deposited; this and the corresponding red Na, K, Rb and Cs compounds are formed by adding copper sulphate solution to excess of alkali pentasulphide solution, filtering, allowing to stand and washing with alcohol. These compounds are usually regarded as *cuprous* compounds derived from H_2S_4, *i.e.* salts of $HCu^{I}S_4$ (Bloxam, *J.C.S.*, 1865, **18**, 94; Hofmann and Höchtlen, 1903; Biltz and Herms, 1907).

Cupric sulphate, commonly known simply as *copper sulphate*, crystallises in large blue triclinic crystals $CuSO_4,5H_2O$, called *blue vitriol* or *bluestone*. It is obtained by dissolving cupric oxide in dilute sulphuric acid. The anhydrous sulphate is formed by heating copper with concentrated sulphuric acid (Glauber, 1648): $Cu + 2H_2SO_4 = CuSO_4 + 2H_2O + SO_2$.

According to Cundall (*J.C.S.*, 1914, **105**, 60; cf. Rogers, *ibid.*, 1926, 254) the latter reaction first forms **cuprous sulphate** Cu_2SO_4; if the acid liquid from 87–94 p.c. H_2SO_4 is cooled, filtered through asbestos in a Gooch crucible and poured into water, a red precipitate of copper is formed: $Cu_2SO_4 = CuSO_4 + Cu$. **Cuprous**

sulphide deposits as a black powder in the earlier stages of reaction, but is afterwards mostly decomposed. The final product is almost entirely anhydrous $CuSO_4$.

1. $8Cu + 4H_2SO_4 = 3Cu_2SO_4 + Cu_2S + 4H_2O$.
2. $2Cu + 2H_2SO_4 = Cu_2SO_4 + 2H_2O + SO_2$.

Secondary reactions then occur :

3. $5Cu_2SO_4 + 4H_2SO_4 = Cu_2S + 8CuSO_4 + 4H_2O$.
4. $Cu_2S + 2H_2SO_4 = CuS + CuSO_4 + 2H_2O + SO_2$.
5. $CuS + 4H_2SO_4 = CuSO_4 + 4SO_2 + 4H_2O$.

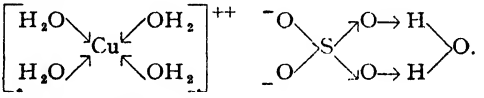
Equations (1) and (3) give Pickering's equation (*J.C.S.*, 1878, **33**, 112) :

$$5Cu + 4H_2SO_4 = Cu_2S + 3CuSO_4 + 4H_2O.$$

Copper sulphate is prepared on the large scale by the action of dilute sulphuric acid on copper in presence of air : $2Cu + 2H_2SO_4 + O_2 = 2CuSO_4 + 2H_2O$, or by the " weathering " of copper pyrites, which may first be roasted :

$$CuS + 2O_2 = CuSO_4.$$

Commercial cupric sulphate usually contains ferrous sulphate, with one form of which, $FeSO_4,5H_2O$, it is isomorphous and forms mixed crystals. In blue vitriol, four molecules of water are attached to the metal ion and one to the sulphate ion by coordinate links :



The solubilities in g. $CuSO_4$/100 g. H_2O are :

0°	15°	25°	30°	50°	60°	80°	100°	104°
14·9	19·3	22·3	25·5	33·6	39·0	53·5	73·5	78·0.

The salt $CuSO_4,5H_2O$ is insoluble in alcohol and is precipitated in small crystals when alcohol is added to the solution. Several crystalline hydrates are known. On exposure to air the blue pentahydrate crystals effloresce to a pale blue powder of $CuSO_4,3H_2O$, which is best made by exposing the pentahydrate over P_2O_5 in a desiccator at 25°–30° for about eleven days till the weight corresponds with trihydrate. The pentahydrate crystals at 100° crumble to a bluish-white powder of monohydrate $CuSO_4,H_2O$. At 220°–260° this loses most of the combined water but 0·04 p.c. is retained even at 360°, and the salt begins to lose sulphur trioxide at higher temperatures before all the water is expelled. Anhydrous $CuSO_4$ is a white powder best prepared by heating powdered ***pure*** $CuSO_4,5H_2O$ (made from electrolytic copper) in a **U**-tube at 240° in a current of dry air until the weight corresponds with $CuSO_4$. If the material contains a trace of iron the product is discoloured.

Copper sulphate is stable to 653° but decomposes completely at 736° : $CuSO_4 = CuO + SO_3$. The white powder obtained by dehydration at 260° is used to detect water in alcohol, ether, etc., when it becomes blue. Anhydrous or hydrated copper sulphate absorbs hydrogen chloride gas and is decomposed by it at 400° or by the aqueous acid : $CuSO_4 + 2HCl = CuCl_2 + H_2SO_4$. This

reaction may be used to separate hydrogen chloride from other gases, such as sulphur dioxide.

Copper sulphate is only slightly hydrolysed: the solution reddens litmus but not methyl orange.

Two definite **basic cupric sulphates** are formed (Weiser, Milligan and Cook, *J.A.C.S.*, 1942, **64**, 503): (i) $4CuO,SO_3,3H_2O$ or $[Cu\{Cu(OH)_2\}_3]SO_4$ by mixing cupric salt and alkali hydroxide solutions with the ratio $\frac{1}{2}Cu^{\cdot\cdot}/OH' = 1{\cdot}25$, and (ii) $5CuO,SO_3,xH_2O$ or $CuSO_4,4CuO,xH_2O$ when the ratio is greater than 1·33. (With the ratio equal to or less than 1, pure cupric hydroxide is precipitated.)

Copper sulphate forms *double salts*, *e.g.* the light blue $K_2Cu(SO_4)_2,6H_2O$ and the lighter blue $(NH_4)_2Cu(SO_4)_2,6H_2O$ and $Na_2Cu(SO_4)_2,2H_2O$, solutions of which may contain small amounts of the complex anion $Cu(SO_4)_2''$. Isomorphous double salts with sulphates of bivalent Mg, Zn, Mn, Fe, Co and Ni crystallise with 5 and $7H_2O$, the cadmium salt with 3 and $5H_2O$. They are usually monoclinic with $7H_2O$ and triclinic with $5H_2O$, like the single salts.

Cupric sulphate forms *ammines* with 5, 4, 2 and $1NH_3$, and corresponding compounds with ND_3 (Hart and Partington, *J.C.S.*, 1943, 104). Deep blue rhombic prisms of $[Cu(NH_3)_4]SO_4,H_2O$ are deposited by adding excess of ammonia to a solution of copper sulphate, pouring a layer of alcohol over the deep blue solution, and allowing to stand in a closed cylinder.

The distribution coefficient of ammonia between ammoniacal copper sulphate solution and chloroform is $k = 31$. If the ammonia concentration in water is c_1, that in chloroform c_2, and c is the cupric ion concentration, $(c_1 - kc_2)/c$ gives the number of molecules of ammonia combined with one cupric ion. Dawson and MacCrae (*J.C.S.*, 1900, **77**, 123; 1901, **80**, 1072; 1906, **89**, 1666) found 3·42–3·7 and Locke and Forssall (*Amer. Chem. J.*, 1904, **31**, 268) 3·94–4·05, hence the ion is $Cu(NH_3)_4^{\cdot\cdot}$.

Cuprous Compounds

Although the analogy with silver and gold suggests that cuprous compounds contain univalent copper, the vapour density of cuprous chloride at 1600°–1700° corresponds with Cu_2Cl_2 and it might contain a complex —Cu—Cu— of bivalent copper, like the mercurous compounds (p. 395). The molecular weight in pyridine, quinoline and fused $BiCl_3$ corresponds with CuCl, but in fused $HgCl_2$ some Cu_2Cl_2 molecules are present. Bodländer and Storbeck (*Z. anorg. Chem.*, 1902, **31**, 1, 458) from very complicated calculations of solubility and E.M.F. measurements concluded that the cuprous ion is $Cu^{\cdot}$ and not $Cu_2^{\cdot\cdot}$, and hence we shall use the simple formulae in what follows. It is doubtful, however, if the simple cuprous ion occurs in appreciable amount in solution, complex ions being usual. Cuprous halides crystallise in zinc blende lattices (p. 242), which supports the simple formula CuX.

Most cuprous compounds are very sparingly soluble and the salts of oxy-acids are generally very unstable, tending to form cupric compounds and metallic copper: $2Cu^{\cdot} = Cu^{\cdot\cdot} + Cu$.

Cuprous hydride CuH is obtained as an unstable brownish-yellow precipitate by heating cupric sulphate solution slightly acidified with sulphuric acid with sodium hypophosphite at 70°, filtering rapidly and washing with hot water (Wurtz, 1844). With excess of hypophosphite the main reaction is (Sieverts, 1909):

$$2Cu^{\cdot\cdot} + 3H_3PO_2 + 3H_2O = 2CuH + 3H_3PO_3 + 4H^{\cdot},$$

but some phosphoric acid is formed. The substance has the composition CuH when moist (Firth and Myers, *J.C.S.*, 1911, **99**, 1329); it loses some hydrogen on drying, but has an X-ray spectrum different from that of copper (Hüttig and Brodkorb, 1926). It evolves hydrogen with concentrated hydrochloric acid.

A cupric hydride described does not exist (Müller and Bradley, *J.C.S.*, 1926, 1669), but black CuH_2 is formed by the action of atomic hydrogen on roughened copper (McMahon and Robinson, *J.C.S.*, 1934, 854).

Cuprous oxide Cu_2O or *red oxide of copper* is formed on strongly heating a mixture of cupric oxide and copper filings, but is usually prepared by the partial reduction of cupric compounds in alkaline solution.

EXPT. 1.—Dissolve 69 g. of pure copper sulphate crystals in 1 litre of water, adding 1 drop of sulphuric acid (*Solution A*). Dissolve in 1 litre of water 350 g. of Rochelle salt (sodium potassium tartrate $NaKC_4H_4O_6.4H_2O$) and 100 g. of caustic soda (*Solution B*). Mix together 25 c.c. of *A* and 25 c.c. of *B*: the resulting deep blue liquid is called **Fehling's solution**. Boil this in a porcelain dish with a solution of glucose (grape sugar). A yellow precipitate is deposited which quickly turns to bright red *cuprous oxide*. Filter, wash with boiling water and then with alcohol, and dry in a steam-oven.

The yellow precipitate first formed is shown by X-ray analysis to be finely divided Cu_2O and not CuOH (Straumanis and Cirulis, 1935).

A thin film of cuprous oxide formed on copper by heating in air is used as a current rectifier and in photoelectric cells (*J.S.C.I.*, 1932, **51**, 446R).

Cuprous oxide colours a borax bead red and is used to make the cheaper kind of ruby glass. It is also used, with cupric oxide, in painting ships. Cuprous oxide is basic and dissolves in concentrated hydrochloric acid to form cuprous chloride (or a complex acid H_2CuCl_3); since cuprous sulphate and nitrate are decomposed by water, it reacts with dilute sulphuric acid to form a solution of cupric sulphate and metallic copper: $Cu_2O + H_2SO_4 = CuSO_4 + Cu + H_2O$, and with cold 10 p.c. nitric acid to form a solution of cupric nitrate and copper: $Cu_2O + 2HNO_3 = Cu(NO_3)_2 + Cu + H_2O$; on heating or with more concentrated nitric acid the copper dissolves and nitric oxide is evolved: $3Cu_2O + 14HNO_3 = 6Cu(NO_3)_2 + 2NO + 7H_2O$. Cuprous oxide dissolves in ammonia to a colourless solution if free oxygen is excluded, otherwise a blue solution containing a cupric compound (p. 336) is formed.

An olive-green **copper suboxide** Cu_4O precipitated from cupric sulphate solution by sodium stannite solution (Rose, 1863) contains stannic oxide and may be a variable mixture of cuprous oxide and copper (Moser, 1909), although it dissolves completely in dilute sulphuric acid to a colourless solution which in a few seconds becomes purple and deposits metallic copper.

Cuprous fluoride CuF is formed as a red crystalline solid, m.p. 908°, by heating CuCl or CuF_2 at 1100° in hydrogen fluoride gas. It sublimes at 1200° and is decomposed by water into CuF_2 and copper (Poulenc, 1894).

Cuprous chloride, bromide and iodide form white tetrahedral crystals, and are sparingly soluble: cuprous chloride is partly decomposed by pure water into cupric chloride and copper and is also hydrolysed. The solubilities in mols/lit. at 25° are given as:

CuCl $1{\cdot}1 \times 10^{-3}$ CuBr $2{\cdot}0 \times 10^{-4}$ CuI $2{\cdot}25 \times 10^{-6}$ (CuCNS $5{\cdot}5 \times 10^{-7}$).

The m.ps. are CuCl 422°, CuBr 480°, CuI 605° (the melts are electrolytes), and the b.ps. CuCl 1366°, CuBr 1345°, CuI 1290°.

Cuprous chloride CuCl occurs native as *nantoquite* in Chile. It was obtained by Boyle in 1666 as a brown resinous mass (*resin of copper*), turning green in moist air, by heating copper with mercuric chloride:

$$2Cu + HgCl_2 = 2CuCl + Hg$$

It is formed (together with some cupric chloride) when copper burns in a limited supply of chlorine. Cuprous chloride is formed by heating cupric chloride: $2CuCl_2 = 2CuCl + Cl_2$, and by passing hydrogen chloride over heated copper: $2Cu + 2HCl = 2CuCl + H_2$.

Copper powder dissolves in hot concentrated hydrochloric acid and copper foil slowly, with evolution of hydrogen (Tilden, *J.S.C.I.*, 1886, **5**, 84); a solution of cuprous chloride is more easily formed if some nitric acid or potassium chlorate is added to the hydrochloric acid (Lupton, 1874).

A solution of cupric chloride in concentrated hydrochloric acid is reduced to cuprous chloride by zinc dust (Heumann, 1874): $CuCl_2 + H = CuCl + HCl$, or by boiling with copper turnings till the solution is colourless:

$$CuCl_2 + Cu = 2CuCl,$$

and on pouring into water white cuprous chloride precipitates.

EXPT. 2.—Dissolve 25 g. of cupric oxide in 250 c.c. of concentrated hydrochloric acid in a flask. Add 50 g. of copper turnings and boil in a fume-cupboard until the solution is colourless. Pour into a litre of previously boiled distilled water, filter in a Buchner funnel, wash rapidly with water containing sulphur dioxide (to prevent oxidation), then with alcohol and finally with a little ether, and dry on a porous plate in a vacuum desiccator.

A convenient method of preparation (Péan de St. Gilles, 1854; Wöhler, 1864) is to reduce a solution of cupric chloride with sulphur dioxide:

$$2CuCl_2 + SO_2 + 2H_2O = 2CuCl + H_2SO_4 + 2HCl.$$

EXPT. 3.—Pass sulphur dioxide into a solution of 25 g. of copper sulphate crystals and 12 g. of sodium chloride in 70 c.c. of water till the solution, even on standing, smells strongly of SO_2. Cuprous chloride crystallises and more separates on boiling the filtrate. Treat as in Expt. 2.

Cuprous chloride is a white powder and crystallises from concentrated hydrochloric acid in white tetrahedra. It melts at 422° and forms a brown resinous mass on cooling. When exposed moist to light it darkens (cf. AgCl) and in moist air it forms green basic cupric chloride $CuCl_2,Cu(OH)_2,H_2O$. It combines with ammonia gas forming compounds of CuCl with 3, $1\frac{1}{2}$ and $1NH_3$ and dissolves readily in ammonia forming a colourless solution in absence of oxygen (*e.g.* in presence of copper in a closed bottle), and crystals of $Cu(NH_3)Cl,H_2O$ deposit on cooling a solution of copper powder in boiling ammonium chloride solution. An ammoniacal solution of cuprous chloride is used in gas analysis to absorb carbon monoxide and acetylene. Acetylene gives a bright red precipitate of Cu_2C_2 (p. 454), explosive when dry and evolving acetylene when warmed with concentrated hydrochloric acid: $Cu_2C_2 + 2HCl = 2CuCl + C_2H_2$. Cuprous chloride dissolves in solutions of cupric salts, thiosulphate solution, and pyridine.

The colourless solution in hydrochloric acid (in absence of oxygen) probably contains the complex acids $HCuCl_2$ and H_2CuCl_3, salts of which (*e.g.* $KCuCl_2,H_2O$ and K_2CuCl_3) are known. It rapidly becomes green or yellow on exposure to air: $4CuCl + 4HCl + O_2 = 4CuCl_2 + 2H_2O$. It absorbs carbon monoxide, forming a solution of an unstable compound $CuCl,CO,2H_2O$ (Jones, *Amer. Chem. J.*, 1899, **22**, 287; Manchot and Friend, *Annalen*, 1908, **359**, 100); the anhydrous compounds Cu(CO)Cl and Cu(CO)Br are formed only under pressure with the solids (Wagner, 1931). A solution of cuprous chloride in hydrochloric acid absorbs phosphine and forms $Cu(PH_3)Cl$.

Cuprous bromide CuBr is formed with incandescence on heating bromine with excess of copper; copper dissolves in hot concentrated hydrobromic acid with evolution of hydrogen and the solution deposits white cuprous bromide when poured into water. It is most conveniently prepared by passing sulphur dioxide into a solution of 20 g. of copper sulphate crystals, 8 g. of sodium bromide and 300 c.c. of water, as in Expt. 3.

Cuprous iodide CuI occurs as *marshite* at Broken Hill, Australia. It is formed by heating copper in iodine vapour. Copper dissolves in hot concentrated hydriodic acid with evolution of hydrogen and the solution deposits cuprous iodide when poured into water. On adding alkali iodide solution to copper sulphate solution a green precipitate which may be cupric iodide (Walker and Dover, *J.C.S.*, 1905, **87**, 1584, say it contains CuI_4) is formed but soon decomposes into white CuI and free iodine:

$$2CuSO_4 + 4KI = 2CuI + 2K_2SO_4 + I_2.$$

Addition of sulphur dioxide, sodium thiosulphate or ferrous sulphate prevents the formation of iodine:

$$2CuSO_4 + 2KI + SO_2 + 2H_2O = 2CuI + K_2SO_4 + 2H_2SO_4$$
$$2CuSO_4 + 2KI + 2FeSO_4 = 2CuI + Fe_2(SO_4)_3 + K_2SO_4.$$

EXPT. 4.—Dissolve 10 g. of $CuSO_4.5H_2O$ and 12·5 g. of $FeSO_4.7H_2O$ in 250 c.c. of water and add 7·0 g. of KI in 75 c.c. of water. Filter, wash and dry

the 7·5 g. of CuI formed. It retains water obstinately. The reaction with SO_2 as in Expt. 3 may also be used.

Cuprous iodide becomes red and then black on heating, but becomes white on cooling. It is sparingly soluble in water and alkali iodide solutions, but readily soluble in ammonia (the solution absorbs CO), and in cyanide and thiosulphate solutions.

Since cuprous oxide is only weakly basic no *cuprous carbonate* is known.

Copper dissolves in alkali cyanide solution in absence of oxygen and in contact with platinum hydrogen is briskly evolved :

$$2Cu + 8KCN + 2H_2O = 2K_3Cu(CN)_4 + 2KOH + H_2.$$

Cuprous cyanide CuCN, m.p. 474·5°, is formed as a white precipitate on adding alkali cyanide to a cupric salt solution, cyanogen being evolved unless a reducing agent such as sulphite is present (cf. CuI) :

$$2Cu^{\cdot\cdot} + 4CN' = 2CuCN + C_2N_2$$
$$2Cu^{\cdot\cdot} + 2CN' + SO_3'' + H_2O = 2CuCN + H_2SO_4.$$

Cuprous cyanide dissolves in excess of alkali cyanide to form the very stable complex ion $Cu(CN)_4'''$, not precipitated by hydrogen sulphide. This is used in the separation of copper and cadmium in analysis (p. 171). Excess of cyanide is added to repress the ionisation of $Cu(CN)_4'''$ and hydrogen sulphide passed in : only cadmium sulphide is precipitated.

The solid compounds $K[Cu(CN)_2]$, $K_3[Cu(CN)_4]$ and $K[Cu_2(H_2O)(CN)_3]$ are known (Bassett and Corbett, *J.C.S.*, 1924, **125**, 1660).

A blue solution of cupric salt in ammonia is decolorised by cyanide and the solids $[Cu^{II}(NH_3)_3][Cu^{I}(CN)_2]_2$ and $[Cu^{II}\,en_2][Cu^{I}(CN)_2]_2,H_2O$ are known (Schmidt, 1898 ; Morgan and Burstall, *J.C.S.*, 1926, 2018.

A white precipitate of the very sparingly soluble **cuprous thiocyanate** CuCNS (insoluble in hydrochloric acid) is formed on adding potassium or ammonium thiocyanate to a solution of cupric sulphate containing ferrous sulphate or sulphur dioxide :

$$2CuSO_4 + 2FeSO_4 + 2KCNS = 2CuCNS + Fe_2(SO_4)_3 + K_2SO_4$$
$$2CuSO_4 + SO_2 + 2H_2O + 2KCNS = 2CuCNS + 2H_2SO_4 + K_2SO_4.$$

Cuprous nitrate is known only in coordination compounds, *e.g.* (tu = thiourea, etu = ethylene thiourea) : $[Cu(NH_3)_2]NO_3$ (Sloane, *J.A.C.S.*, 1910, **32**, 972), $[Cu_2\,tu_5](NO_3)_2,2H_2O$, $[Cu\,tu_2]NO_3,H_2O$, $[Cu\,etu_4]NO_3$ (Morgan and Burstall, *J.C.S.*, 1928, 143).

Cuprous sulphide, Cu_2S, the stable sulphide of copper, is formed when copper burns in sulphur vapour, as when sulphur is heated in a flask with copper turnings ; it is obtained pure by heating in vacuum to the m.p. 1135°. It is formed by heating cupric sulphide in a current of hydrogen or carbon dioxide (Pickering, *J.C.S.*, 1881, **39**, 401) : $2CuS = Cu_2S + S$, or by precipitating with hydrogen sulphide a solution of cuprous chloride in hydrochloric acid. It is only slowly decomposed by chlorine at a red heat and is scarcely attacked by

fused sodium carbonate ; by fusion with alkali sulphides it forms steel-blue crystalline insoluble **thiocuprites** *e.g.* K[CuS] and $Na_2[Cu_4S_3]$ (Bodländer, 1905).

Cuprous sulphite is present in the red crystalline *Chevreul's salt* (1812) $Cu^{II}[(Cu^{I}SO_3)_2],2H_2O$, prepared by passing sulphur dioxide into a solution of cupric acetate in acetic acid and boiling (Millon and Commaille, *Compt. rend.*, 1863, **57**, 820) :

$$4Cu(CH_3CO_2)_2 + 3SO_2 + 4H_2O = Cu[(CuSO_3)_2] + CuSO_4 + 8CH_3COOH.$$

Cuprous sulphate is at once decomposed by water, and can be prepared only in its absence : $Cu_2SO_4 = Cu + CuSO_4$. It is formed by heating cuprous oxide with dimethyl sulphate at 160° : $Cu_2O + (CH_3)_2SO_4 = Cu_2SO_4 + (CH_3)_2O$, washing the white powder with ether and drying in vacuum (Recoura, 1909). Its compounds with ammonia $[Cu_2(NH_3)_4]SO_4,H_2O$ and thiourea $[Cu_2\,tu_5]SO_4,2H_2O$ are more stable. A white crystalline compound $Cu_2SO_4,2CO,H_2O$ is formed by passing carbon monoxide into an ammoniacal solution of cupric sulphate.

Silver

Silver was known in Predynastic Egypt (4000 B.C.) but was very rare, and there is a fine Chaldaean silver vase of 2850 B.C. in the Louvre. The oldest silver probably came from North Syria and Asia Minor and the Hittites played an important part in its metallurgy. Silver mines in Spain were worked at an early date.

Silver occurs native, often in large masses, in Norway, Chile, Peru and Idaho, occasionally nearly pure but usually containing copper and gold. Important ores are the sulphide *argentite* (or *silver glance*) Ag_2S (the commonest ore), *chlorargyrite* (or *horn-silver*) AgCl, *pyrargyrite* (or *ruby-silver*) Ag_3SbS_3, *stromeyerite* (or *silver-copper glance*) $(Cu,Ag)_2S$, and *stephanite* Ag_5SbS_4. Less important are *proustite* Ag_3AsS_3, the bromide AgBr and the iodide AgI. Traces of silver occur in sea water (Proust, 1787).

The principal producers of silver are the United States, Mexico, Peru, Bolivia, and the Cobalt mines in Ontario ; the rest comes mostly from Europe, New South Wales (Broken Hill) and Japan. Much silver is extracted from ores of other metals (*e.g.* of lead, copper and zinc) and from the anode slimes of copper refining (p. 329).

Silver is extracted from its ores by :

(i) alloying with lead and removing the lead by oxidation (*cupellation*), the silver-lead alloy being first enriched by the (almost obsolete) *Pattinson process* in which nearly pure lead is crystallised from the molten alloy, or by dissolving the silver in fused zinc in the *Parkes process* ;

(ii) amalgamation with mercury and separation of the mercury by distillation in the (almost obsolete) *Mexican process* ;

(iii) dissolving by dilute alkali cyanide in presence of oxygen, and precipitation by zinc (*cyanide process*, an important *wet process*).

The **cupellation process** was in ancient use. The silver ore is smelted with a lead ore and the alloy of silver and lead treated to separate the silver. The lead from galena is nearly always argentiferous and is an important source of silver. It is desilvered by the Pattinson or Parkes process (*q.v.*). The rich alloy is then melted on a flat **cupel** or *test* of bone ash or (usually) clay and limestone or barytes, or cement. A blast of air driven over the surface of the metal (Fig. 180) oxidises the lead to litharge PbO, which fuses, dissolves any copper

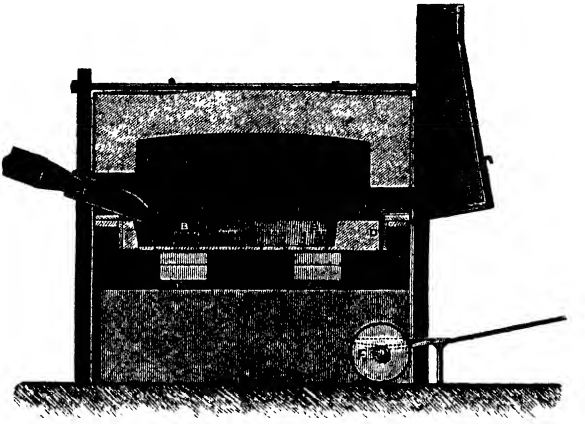


FIG. 180.—Cupellation furnace.

oxide, etc., and is swept away by the blast, the last portions being absorbed by the porous cupel, and bright silver is left.

When the metal contains 60–70 p.c. Ag, the temperature is raised from 800° to 1000° and a little sodium nitrate added to remove impurities. In the last stage the litharge film becomes so thin that iridescent colours are seen and the bright silver surface "flashes." The final metal contains 99·5 p.c. of silver.

The Pattinson process (1833).—On cooling fused argentiferous lead, nearly pure lead separates at a temperature below the f.p. of lead, because of the depression of freezing point by dissolved silver. The crystals of lead are withdrawn by perforated iron ladles and the liquid alloy is enriched in silver until (if the process were carried far enough) lead and silver would separate together. The Ag-Pb system belongs to Roozeboom's Type III (Fig. 34) with a minimum at 303°, when the liquid contains **2·25** p.c. of Ag. In practice, seven-eighths of the lead are removed. The process is carried out in a row of iron pots, the separated lead being passed from pot to pot to be remelted, and the liquid alloy passed in the other direction. The silver accumulates in the alloy at one end and desilvered lead (0·001–0·002 p.c. Ag) at the other. The rich alloy is then cupelled.

In the Luce-Rozan process (1873) only two pots are used, an upper or melting pot and a lower or crystallising pot, holding 7 and 21 tons respectively. The

lead is deposited in the crystallising pot by blowing steam at 50 lb. pressure through the fused metal, whilst cold water is sprayed on the surface. When two-thirds of the lead have separated, the liquid is strained off through a perforated plate. The separated lead is remelted and the process repeated.

The Parkes process (1850).—Molten lead dissolves only 1·6 p.c. of zinc and molten zinc 1·2 p.c. of lead (the miscibility becomes complete at 935°). If 1–2 p.c. of zinc is added to molten lead containing silver, the zinc dissolves the silver (and some lead) and the alloy floats to the surface and solidifies on cooling. A second lot of zinc is added. The crust is skimmed off with a perforated ladle and strongly heated with carbon in a fireclay retort, when zinc distils and lead containing 3·5–4 p.c. of silver remains and is cupelled. The zinc-silver-lead alloy may also be electrolysed as anode in zinc chloride solution, when zinc dissolves and deposits on the cathode. To remove traces of zinc from the desilvered lead it is heated to redness and steam forced through the molten metal, when zinc oxide rises to the surface. For a ton of lead containing 14 oz. of silver, 22·4 lb. of zinc are required. The Parkes process (proposed by Karsten in 1842) has superseded the Pattinson process.

Any gold and copper are removed by the zinc. The desilvered lead contains only 0·0004 p.c. of silver. If bismuth is present (which may be objectionable and is difficult to remove from the lead) it goes to the argentiferous part in the Pattinson process, but remains in the lead in the Parkes process, which is then less suitable.

Amalgamation and wet processes.—The *amalgamation process* was first used in Mexico, where fuel is scarce, by Bartolomeo de Medina in 1557. Since 1904 it has gradually been replaced by the cyanide process.

The ores containing metallic silver, silver chloride and sulphide and a large quantity of rock, are finely crushed in stamping mills, and the fine mud, mixed with a little salt, is well trodden by mules on a paved floor or *patio*. Mercury is added with a little roasted pyrites, containing cupric and ferric sulphates, and the treading is continued for fifteen to forty-five days. According to Percy, cuprous chloride is first formed and then decomposes the silver sulphide :

$$2Ag_2S + 8CuCl + 3O_2 + 6H_2O = 4AgCl + 2S + 2\{CuCl_2,3Cu(OH)_2\}.$$

The silver chloride dissolves in the brine and is reduced by the finely divided mercury : $AgCl + Hg = Ag + HgCl$. The silver forms an amalgam with the excess of mercury (About 1 p.c. of sodium is added to the mercury to prevent the formation of a fine powder, which would be lost in washing.) The amalgam is separated by washing, the calomel being lost, the excess of mercury is pressed out from the amalgam in canvas bags, and the residue is distilled in iron retorts to recover the mercury

In *Ziervogel's wet process* the ore is roasted at 850° when soluble silver sulphate is formed and is lixivated, the silver being precipitated from the solution by copper. Anode slimes from copper refining are roasted to convert copper to sulphate, extracted with water, and the residue cupelled or smelted in a basic reverberatory furnace with fluxes. In the modern **cyanide process** the unroasted

ore or concentrate, finely ground in ball mills, is leached with 0·4 p.c. sodium cyanide solution, the slime being well agitated by a stream of air. Soluble **sodium argentocyanide** $NaAg(CN)_2$ is formed :

$$4Ag + 8NaCN + 2H_2O + O_2 = 4NaAg(CN)_2 + 4NaOH$$
$$Ag_2S + 4NaCN \rightleftharpoons 2NaAg(CN)_2 + Na_2S.$$

The sodium sulphide is oxidised ultimately to sulphate by aeration :

$$4Na_2S + 5O_2 + 2H_2O = 2Na_2SO_4 + 4NaOH + 2S.$$

A side reaction is :

$$2Na_2S + 2NaCN + O_2 + 2H_2O = 2NaCNS + 4NaOH.$$

The silver is precipitated from the solution by zinc :

$$2NaAg(CN)_2 + Zn = 2Ag + Na_2Zn(CN)_4,$$

or else the silver is precipitated by sodium sulphide and the silver sulphide reduced by caustic soda solution and aluminium ingots in a revolving cylinder :

$$3Ag_2S + 8NaOH + 2Al = 6Ag + 3Na_2S + 2NaAlO_2 + 4H_2O.$$

Silver is refined by cupellation, and, if it contains gold, by the **Moebius electrolytic process** (1884). The electrolyte is silver nitrate solution with about 1 p.c. of free nitric acid ; the cathode is a plate of pure silver and the anode a block of the silver to be refined. Silver is deposited, copper dissolves, and gold deposits as a slime which collects in a canvas bag round the anode. The copper must not accumulate in the solution beyond 4–5 p.c.

Commercial silver is alloyed with copper, as the pure metal is too soft for coinage or jewellery. The proportion of silver in 1000 parts of alloy is called the *fineness*. British *fine silver* contains 925, United States 900, of silver in 1000 parts. British silver coin now contains 50 p.c. of silver, the rest being mostly nickel with a little copper. Cadmium makes silver easier to work.

Silver goods are sometimes treated by heating in air and removing the copper oxide formed by dilute acid, leaving a pure silver surface.

The old *Sheffield plate* was made by laying a strip of silver on a copper bar, heating and rolling. Copper plated with gold occurs in ancient Egyptian and Babylonian remains and later Roman coins were silver-plated copper. Copper is *electroplated* with silver by making it the cathode in a solution of silver cyanide in excess of alkali cyanide, with a pure silver plate as anode. The solution contains $Ag(CN)_2'$ ions, slightly dissociated : $Ag(CN)_2' \rightleftharpoons Ag^{\cdot} + 2CN'$. The $Ag^{\cdot}$ ions deposit as a coherent film instead of crystals and the CN' ions discharged on the anode form AgCN, which dissolves in the solution. Bright deposits are formed if carbon disulphide is added to the bath. A compound of silver nitrate and thiourea can replace the poisonous cyanide bath (Gockel, 1934).

Pure silver is prepared from alloy containing copper by dissolving in dilute nitric acid, diluting, precipitating silver chloride with hydrochloric acid, filtering and washing with hot water and reducing the silver chloride in one of the following ways :

(*a*) The dry chloride is fused in a crucible with sodium carbonate, when a button of pure silver is formed : $4AgCl + 2Na_2CO_3 = 4Ag + 4NaCl + 2CO_2 + O_2$.

(*b*) The moist chloride is boiled with sodium hydroxide solution and grape-sugar : the oxide first formed is converted into a grey powder of metallic silver, which is washed with boiling water.

(*c*) Dilute sulphuric acid is poured over moist silver chloride and a stick of pure zinc placed in the mixture. The chloride is reduced by nascent hydrogen forming a grey mass of silver powder (*molecular silver*), which is washed and dried.

The silver from (*b*) or (*c*) may be fused (m.p. 960·5°) with sodium carbonate to form a button. (If silver is fused in a glazed porcelain crucible this becomes yellow, owing to the formation of silver silicate.) Stas distilled silver in a quick-lime retort with the oxy-hydrogen blowpipe. Richards and Wells (*J.A.C.S.*, 1905, **27**, 459) showed that Stas's silver contains a little occluded oxygen, which may be removed by fusion on lime in an atmosphere of hydrogen, but the metal then contains a trace of calcium formed by reduction of the lime (Baxter and Lundstedt, *J.A.C.S.*, 1940, **62**, 1829).

Fused silver dissolves oxygen (perhaps as oxide) and gaseous oxygen is mostly liberated as the metal solidifies. The crust is violently disturbed and the metal " spits," part of the liquid metal being forced out as excrescences. This phenomenon, mentioned by Pliny, is a good test of the completion of cupellation : it is prevented by covering the metal with charcoal powder. One g. of silver at 1024° dissolves 2·05 c.c. of oxygen, measured at S.T.P.

Properties of silver.—Silver is pure white, malleable and ductile : it can be beaten into leaves 0·00025 mm. thick, which become somewhat transparent on heating. Very thin films on glass transmit blue light. It is the best conductor of heat and electricity of all metals, copper being next. The m.p. is 960·5° in absence of air and 956° in air, the b.p. is 1955°. The vapour is pale blue and monatomic.

Although pure silver is not affected by pure air or oxygen it tarnishes in ordinary air to a film of sulphide, this being yellow, blue and black with increasing thickness. It is formed by hydrogen sulphide in the air in presence of oxygen (pure H_2S does not affect silver) (Lilienfeld and White, *J.A.C.S.*, 1930, **52**, 885) : $4Ag + 2H_2S + O_2 = 2Ag_2S + 2H_2O$. Silver spoons are similarly stained by organic sulphur compounds in eggs.

In presence of dissolved oxygen silver dissolves in distilled water to the extent of about 0·037 mg. per litre and about 0·003 mg. more in a glass vessel :

$$2Ag + H_2O + \tfrac{1}{2}O_2 = 2Ag^{\cdot} + 2OH'.$$

Silver is attacked by chlorine and more slowly by bromine, iodine and sulphur. The powder dissolves in hot concentrated hydriodic acid with evolution of hydrogen. Silver is not attacked by hydrochloric or dilute sulphuric acids ; it dissolves in boiling concentrated sulphuric acid or cold dilute nitric acid, but resists the action of alkalis, even fused.

Silver is deposited by reduction on glass in the manufacture of mirrors.

EXPT. 5.—Clean a test-tube with boiling nitric acid, wash well with water, and prepare in it a dilute solution of silver nitrate. Add *dilute* ammonia drop by drop until the precipitate of silver oxide is *almost* redissolved. Then add a solution of caustic potash and Rochelle salt. Place the tube in a beaker of water and heat to boiling. A mirror of silver is deposited. With acetaldehyde or glucose a mirror is formed in the cold (Wood, *J.S.C.I.*, 1896, **15**, 19; Sugden, *J.C.S.*, 1933, 770).

Colloidal silver may be prepared by striking arcs between silver wires under water or by reduction. With ferrous sulphate in presence of sodium citrate a lilac precipitate is formed, which dissolves in pure water to a red transparent solution.

Carey Lea (1889–91) considered these to be allotropic modifications, but the X-rays show that the particles are crystalline. By heating silver nitrate with alkaline sodium protalbate or lysalbate, Paal (1902) prepared a yellow solution of colloidal silver. If this is dialysed and evaporated on a water bath, a brownish-black powder is formed containing as much as 93 p.c. of silver and soluble in water to a dark coloured colloidal solution (*protargol* and *collargol*) used in eye treatment.

SILVER COMPOUNDS

Silver differs from copper in showing no tendency to form basic salts (since silver oxide is a very strong base), and in showing almost entirely univalency. The soluble univalent compounds are electrovalent and give the normal ion $Ag^{\cdot}$. Optical activity is shown in 4-covalent compounds with 8-hydroxyquinoline (Hein, 1935–6). Compounds of univalent silver will first be described.

A white salt-like **hydride** AgH, stable up to 500°, is formed by the prolonged action of atomic hydrogen on silver foil (Pietsch, etc., 1931).

Silver oxide (*argentous oxide*) Ag_2O is formed from finely divided silver and oxygen at 300° under 15 atm. pressure: $4Ag + O_2 \rightleftharpoons 2Ag_2O$, but is usually prepared by adding potassium, sodium or barium hydroxide solution to a solution of silver nitrate. The brown precipitate becomes almost black on drying at 60°–80°, but cannot be freed from water (Baker and Riley, *J.C.S.*, 1926, 2510). It is also formed by boiling silver chloride with sodium hydroxide solution.

The **hydroxide** AgOH is not formed from aqueous solution; it is said to be precipitated from alcoholic silver nitrate and potassium hydroxide solutions at −30°, but is very unstable. Moist silver oxide reacts as if it were the hydroxide.

Silver oxide is slightly soluble (0·021 g./lit. at 25°) in water to an alkaline solution; the moist solid absorbs atmospheric carbon dioxide to form silver carbonate, and precipitates many metals (Cu, Zn, Cd, Hg, Al, Bi, Cr, Fe, Ni, etc.) as oxides or hydroxides from solutions of salts. Silver oxide loses oxygen at 250° and is completely decomposed at 300° (Lewis, *J.A.C.S.*, 1906, **28**, 139;

Rørdam, *Z. phys. Chem.*, 1921, **99**, 474); the reaction is reversible: $2Ag_2O \rightleftharpoons 4Ag + O_2$. It is reduced by hydrogen and carbon monoxide even at room temperature.

Silver oxide dissolves in ammonia and on exposure to air the solution deposits a black precipitate of *fulminating silver*, containing **silver nitride** Ag_3N (or Ag_2NH), very explosive when dry (Raschig, 1886; Olmer and Dervin, 1924).

A **silver suboxide** Ag_4O is said to be formed by the action of steam at 180° on the subfluoride Ag_2F.

Silver Halides

AgF, yellow, m.p. 435°. AgCl, white, m.p. 455°, b.p. 1550°.
AgBr, pale yellow, m.p. 422°. AgI, yellow, three forms, m.p. 552°.

The *solubilities* in mg./lit. at 25° are:

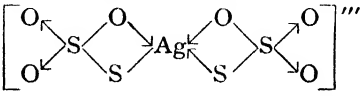
	AgCl	AgBr	AgI
In water - - -	2	0·133	0·0023
In 10 p.c. ammonia -	46·8	3·32	0·036

Silver fluoride AgF is the only soluble silver halide. Hydrofluoric acid does not attack silver but dissolves the oxide and on evaporation in vacuum deposits yellow crystals of AgF,H_2O which cannot be completely freed from water on heating. On fusion and cooling an elastic black mass is formed, containing some silver: $4AgF + 2H_2O = 4Ag + 4HF + O_2$. It is easily cut with scissors. The solution is hydrolysed. Acid fluorides $AgHF_2$ and AgH_3F_4 are described.

Silver subfluoride Ag_2F, which is bright yellow, crystalline and electrically conducting, is formed by heating a solution of AgF with silver powder, or by the electrolysis of AgF. It has a characteristic X-ray spectrum (Hettich, *Z. anorg. Chem.*, 1927, **167**, 67; 1928, **170**, 107; Terrey and Diamond, *J.C.S.*, 1928, 2820; Scholder and Traulsen, *Z. anorg. Chem.*, 1931, **197**, 57).

Silver chloride occurs native as *horn-silver* (cubic). It was described as *luna cornea* by Oswald Croll (1608), who says it was used by the alchemists in the fraudulent transmutation of lead into silver. It is formed on heating silver in chlorine or hydrogen chloride, but is more readily prepared as a curdy white precipitate by adding hydrochloric acid or a chloride to a solution of silver nitrate. It readily fuses to a dark-yellow liquid which solidifies on cooling to a soft colourless tough mass, and volatilises at a white heat, the vapour density corresponding with AgCl. The solubility in water is very small, but it dissolves slightly in dilute nitric acid on standing and in 200 parts of concentrated hydrochloric acid. It is not decomposed by cold, but dissolves in boiling concentrated sulphuric acid: $2AgCl + H_2SO_4 = Ag_2SO_4 + 2HCl$. It dissolves fairly easily in sodium chloride solution and readily in ammonia, forming the complex ion $Ag(NH_3)_2^{\cdot}$. The solid forms compounds with 3, 2, 1½, 1 and ½NH_3. Silver chloride also dissolves in solutions of alkali cyanide (p. 348) and mercuric nitrate, and readily in sodium thiosulphate solution

forming a complex ion $Ag(S_2O_3)_2'''$, with a sweet taste but poisonous (Slator, *J.C.S.*, 1905, **87**, 481 ; Bassett and Lemon, *J.C.S.*, 1933, 1432) :



Silver chloride is reduced by heating in hydrogen : $2AgCl + H_2 \rightleftharpoons 2Ag + 2HCl$.

Silver bromide AgBr forms a pale yellow precipitate insoluble in dilute nitric acid and only sparingly soluble in *dilute* ammonia but readily in concentrated.

Silver iodide AgI forms a light yellow precipitate insoluble in dilute nitric acid and only very sparingly soluble in concentrated ammonia (which changes its colour to white), but soluble in sodium thiosulphate, hydriodic acid and saturated potassium iodide solution.

Silver iodide *contracts* on heating from – 10° to 70° (Fizeau, 1869 ; Jones and Jelen, *J.A.C.S.*, 1935, **57**, 2532). Although the chloride and bromide crystallise in rock salt cubic lattices the iodide is trimorphous (Helmholz, *J. Chem. Phys.*, 1935, **3**, 740 ; Strock, *Z. phys. Chem.*, 1934, **25B**, 441), crystallising in wurtzite, zinc blende, and (above 146°) cubic lattices. It is incompletely reduced by hydrogen even at high temperatures.

When chlorine is passed into water containing suspended silver oxide, silver chloride and hypochlorous acid are formed :

$$Ag_2O + 2Cl_2 + H_2O = 2AgCl + 2HOCl.$$

The hypochlorous acid dissolves excess of silver oxide to form a solution of **silver hypochlorite**, fairly stable in presence of silver oxide. The settled liquid rapidly deposits silver chloride and forms a solution of **silver chlorate**, which may be crystallised, and dried at 150° (Stas) : $3AgOCl = 2AgCl + AgClO_3$. It melts at 230° and decomposes at 270° : $2AgClO_3 = 2AgCl + 3O_2$, a trace of chlorine being evolved. It is reduced by sulphurous acid :

$$AgClO_3 + 3SO_2 + 3H_2O = AgCl + 3H_2SO_4.$$

Silver perchlorate $AgClO_4$, m.p. 486°, formed by dissolving the oxide in perchloric acid, is very soluble in water and also dissolves in benzene.

Silver carbonate Ag_2CO_3 is formed as a light yellow precipitate (it is white when pure) from a solution of silver nitrate and alkali carbonate in equivalent amounts, or preferably from silver nitrate solution and one of potassium carbonate and bicarbonate (Schulten, 1887 ; Jeffery and Warrington, *Chem. N.*, 1926, **132**, 373). It loses carbon dioxide at 150°–160° and decomposes completely at 220° : $2Ag_2CO_3 = 4Ag + 2CO_2 + O_2$. The solubility at 25° is $1{\cdot}16 \times 10^{-4}$ mol/lit. and it is almost completely hydrolysed (Spencer and La Pla, 1910 ; Masaki, 1930). White **silver potassium carbonate** $KAgCO_3$ crystallises on cooling a hot concentrated solution of silver nitrate and potassium carbonate (Reynolds, *J.C.S.*, 1898, **73**, 262).

Silver cyanide AgCN is formed as a white precipitate from a silver salt and cyanide solutions ; it dissolves in excess of cyanide to form the complex ion $Ag(CN)_2'$, salts of which, $KAg(CN)_2$, etc., and also the free acid $HAg(CN)_2$, are

known in the solid form. **Silver thiocyanate** AgCNS is formed as a very insoluble white cheese-like precipitate (1×10^{-6} mol/lit. at 20°), insoluble in nitric acid but soluble in KCNS solution, forming the complex salts $KAg(CNS)_2$, $K_2Ag(CNS)_3$ and $K_3Ag(CNS)_4$.

Silver nitrate $AgNO_3$, the commonest silver salt, crystallises from a solution of silver in dilute nitric acid as large transparent rhombic plates, m.p. 209°: $3Ag + 4HNO_3 = 3AgNO_3 + NO + 2H_2O$. A hexagonal form is produced at 158°. The fused salt cast into sticks is called *lunar caustic*. Silver nitrate is very soluble in water: 215 g. at 20°, 400 g. at 50° and 910 g. at 100°, in 100 g. H_2O. The solution is neutral. It also dissolves in alcohol and other organic solvents, the molecular weight being normal in benzonitrile and pyridine.

Silver nitrate is readily decomposed by organic matter such as dust, paper, cork, or the skin, deep black metallic silver being deposited, so that a solution is used in marking linen. The black stain is removed by dilute potassium cyanide solution. The salt is poisonous, but is given internally in small doses in nervous diseases.

Silver nitrate decomposes at 450° into nitrite and oxygen; at high temperature it decomposes completely: $2AgNO_3 = 2Ag + 2NO_2 + O_2$. The decomposition temperature is much higher than that of copper nitrate.

Solid silver nitrate absorbs ammonia gas, forming $Ag(NH_3)_3NO_3$, with evolution of heat. Crystals of $Ag(NH_3)_2NO_3$ separate on evaporating a solution of $AgNO_3$ to which excess of ammonia has been added. Double salts such as $KAg(NO_3)_2$ and $NH_4Ag(NO_3)_2$ are known.

Silver nitrite $AgNO_2$ is formed as a yellowish-white precipitate on mixing solutions of silver nitrate and sodium nitrite. It may be crystallised from hot water. It decomposes on heating: $2AgNO_2 \rightleftharpoons Ag + AgNO_3 + NO$.

Silver orthophosphate Ag_3PO_4 is formed as a pale yellow precipitate (solubility 6 mg./lit. at 20°), containing adsorbed silver nitrate, on adding silver nitrate solution to sodium phosphate solution, the reaction (Bury, *J.S.C.I.*, 1922, **41**, 352T) being:

$$6AgNO_3 + 3Na_2HPO_4 = 2Ag_3PO_4 + 6NaNO_3 + H_3PO_4.$$

White crystals of Ag_2HPO_4 deposit from a solution of Ag_3PO_4 in phosphoric acid. The **pyrophosphate** $Ag_4P_2O_7$ and **metaphosphate** $(AgPO_3)_n$, where n is 2, 3, 6 or 10, are formed as white precipitates from silver nitrate and the sodium salts in solution.

Silver arsenite Ag_3AsO_3, canary-yellow, and **silver arsenate** Ag_3AsO_4, light chocolate-brown (the pure crystals are black), are formed by precipitation (with sodium arsenite solution some $Ag_4As_2O_5$ is also precipitated): the solubilities in mg./lit. at 20° are Ag_3AsO_3 11·5, Ag_3AsO_4 8·5. The arsenite dissolves in potassium hydroxide and in ammonia and on boiling the ammonia solution silver deposits: $2Ag_3AsO_3 + 2NH_3 = 6Ag + As_2O_3 + N_2 + 3H_2O$.

Silver sulphide Ag_2S, m.p. 842°, occurs as *argentite* (cubic) and the rare *acanthite* (rhombic, isomorphous with Cu_2S). The two forms have a transition point at 179°. Silver sulphide is readily formed from the elements or as a black precipitate by hydrogen sulphide from a silver salt solution. When heated in

hydrogen it is reduced to curious threads of silver. The solubility of Ag_2S is very small (p. 168); it is insoluble in ammonia and sodium thiosulphate but dissolves in cyanide solution and in hot dilute nitric acid.

Silver disulphide Ag_2S_2 is said (Hantzsch, 1899) to be precipitated as a brown powder on mixing solutions of sulphur in carbon disulphide and of silver nitrate in benzonitrile.

Silver sulphate Ag_2SO_4 is formed on boiling silver with concentrated sulphuric acid: $2Ag + 2H_2SO_4 = Ag_2SO_4 + SO_2 + 2H_2O$, or by precipitating silver nitrate solution with dilute sulphuric acid, as it is sparingly soluble (0·77 at 17° and 1·46 at 100°, in 100 pts. H_2O). It forms small white rhombic crystals (isomorphous with Na_2SO_4) melting at 652°. It is readily soluble in dilute nitric acid and in concentrated sulphuric acid (from which acid sulphates $HAgSO_4$ and $H_2Ag(SO_4)_2$ can be crystallised). Decomposition begins at 917° and is complete at 923°: $Ag_2SO_4 = 2Ag + SO_2 + O_2$, and reduction occurs on heating in hydrogen or with carbon: $Ag_2SO_4 + C = 2Ag + CO_2 + SO_2$.

Silver sulphite Ag_2SO_3 is formed as a white precipitate, soluble in excess of sulphite forming double salts, *e.g.* $NaAgSO_3,2H_2O$; on boiling the solution alkali dithionate is formed: $2NaAgSO_3 = 2Ag + Na_2S_2O_6$; on heating dry silver sulphite silver dithionate is formed: $2Ag_2SO_3 = 2Ag + Ag_2S_2O_6$.

Silver thiosulphate $Ag_2S_2O_3$ is difficult to obtain pure. Concentrated solutions of silver nitrate and sodium thiosulphate are mixed in equivalent amounts, the grey precipitate is dissolved in ammonia, the filtrate neutralised with nitric acid, and the white precipitate of $Ag_2S_2O_3$ washed and dried. It decomposes on boiling with water: $Ag_2S_2O_3 + H_2O = Ag_2S + H_2SO_4$.

Even sparingly soluble silver salts (AgCl, AgBr, AgI, but not Ag_2S) dissolve in sodium thiosulphate solution and complex thiosulphates are formed. The compounds $Na[Ag(S_2O_3)],H_2O$ and $Na[Ag_3(S_2O_3)_2],H_2O$ are sparingly soluble, but $Na_3[Ag(S_2O_3)_2],2H_2O$ and $Na_5[Ag_3(S_2O_3)_4],2$ or $3H_2O$ are readily soluble (Rosenheim and Trewendt, 1928; Bassett and Lemon, *J.C.S.*, 1933, 1423). The free acid $H[Ag(S_2O_3)],H_2O$ is precipitated in silky needles on adding nitric acid to a solution of $Na[Ag(S_2O_3)]$ in ammonia (Baines, *J.C.S.*, 1929, 2763).

On boiling a silver salt solution with sodium thiosulphate all the silver is precipitated as sulphide:

$$2AgNO_3 + Na_2S_2O_3 + H_2O = 2NaNO_3 + Ag_2S + H_2SO_4.$$

Bivalent Silver

Some compounds of bivalent silver are known. They are dark brown or black and are paramagnetic (Klemm, 1931), since the ion has the same outer structure as the cupric ion and has an odd electron:

$Cu^{\cdot\cdot}$ 2 | 8 | 2 . 6 . 9 |
$Ag^{\cdot\cdot}$ 2 | 8 | 18 | 2 . 6 . 9 |

Some compounds are isomorphous with compounds of bivalent copper and cadmium.

Argentic fluoride AgF_2 is formed by the action of fluorine on silver powder (Ruff, 1934).

Argentic oxide AgO is formed (i) by the action of boiling water on the compound Ag_7NO_{11} (which may contain argentic nitrate) formed in black crystals on the anode in the electrolysis of silver nitrate solution (Watson, *J.C.S.*, 1906, **89**, 578); (ii) by precipitating silver nitrate with potassium or sodium persulphate (Marshall, *J.C.S.*, 1891, **59**, 771; ammonium persulphate reacts differently); (iii) by oxidising Ag_2O with hot alkaline permanganate solution. It was thought to be silver peroxide Ag_2O_2, but Barbieri (1905–7, 1927) showed that its solution in concentrated nitric acid does not reduce MnO_2, PbO_2 or $KMnO_4$, and oxidises iodine to periodic acid.

Anodic oxidation of silver nitrate in presence of pyridine gives the orange-red compound of **argentic nitrate** $[Ag\ py_4](NO_3)_2$ and a series of compounds containing dipyridyl $[Ag\ dipy_2]X_2$, where $X = NO_3$, HSO_4, $\frac{1}{2}S_2O_8$, ClO_3 and ClO_4, and other coordination compounds, are known (Barbieri, 1912, 1932–3; Morgan and Burstall, *J.C.S.*, 1930, 2594).

By anodic oxidation of a solution of AgO in nitric acid the oxide Ag_2O_3 of **tervalent silver** is formed (Barbieri, 1931), and this seems to be contained in the black oxide precipitated with persulphate (Yost, *J.A.C.S.*, 1926, **48**, 152, 374).

Photography.—The blackening of silver chloride on exposure to light was observed by Conrad Gesner (1565) and by Boyle (who explained it as due to the action of air). Scheele (1777) showed that if the black substance is digested with ammonia, unchanged silver chloride is dissolved and a residue of silver remains. He also noticed that violet rays act most strongly, red and orange rays having practically no action. The development of this discovery into photography took place early in the nineteenth century.

In the modern process the light-sensitive medium is usually a suspension or " emulsion " of silver halide in gelatin. High-speed plates and films contain a mixture of silver bromide with a little iodide; process plates, fast lantern plates and bromide papers contain silver bromide; warm-tone " chloro-bromide " papers and lantern plates contain a mixture of chloride and bromide; gas-light papers and lantern plates contain chloride.

The various types of gelatin emulsion are prepared by adding silver nitrate to a solution of gelatin in hot water containing alkali halides in the required proportions. The warm emulsion, after " ripening " for some time, when the silver halide grains increase in size, is allowed to cool and set. The jelly is cut up, washed with water to remove soluble salts, and is then remelted and coated as a thin film on glass (for " plates "), celluloid (for " films "), or on paper having a specially prepared surface. By adding certain dyes (" sensitizers ") the emulsion is made sensitive to rays which do not affect ordinary photographic materials: thus erythrosine makes it sensitive to yellow and green (" orthochromatic "), some cyanine derivatives confer sensitivity to the whole visible spectrum (" panchromatic ") and others to the near infra-red rays which penetrate fog and haze well enough to make long-distance photography possible.

After exposure in the camera a change occurs in the places on the film or plate on which light has fallen. It is *developed* in a solution of a reducing agent such as pyrogallol, hydroquinone, or metol, with alkali and sodium sulphite. The exposed silver halide is reduced to black metallic silver :

$$C_6H_4(OH)_2 + 2AgBr = C_6H_4O_2 + 2Ag + 2HBr.$$

The unchanged halide is then removed by *fixing* in a solution of sodium thiosulphate.

To prevent over-vigorous development, when some unexposed halide is reduced and causes " fogging ", potassium bromide is added to the developer. It retards development by lowering the solubility of the silver bromide or chloride. *Desensitizers* are dyes (usually of the safranine class) which when dissolved in the developer solution enable development to be carried out in fairly bright artificial light instead of the very dim red or green light usually employed. Positive prints are usually made on bromide or gaslight papers, which are exposed, developed, and fixed in the same way as plates.

Sheppard (1925) found that the very high speed of photographic emulsions is due to traces (1 in 100,000 to 300,000) of organic sulphur compounds in the gelatin. Sheppard and Trivelli (1926–1928) consider that minute nuclei of silver and silver sulphide (" sensitivity specks ") present in silver halide crystals play an important part, electrolytic action being set up on exposure to light which enlarges the nuclei so that they may become centres of development.

The exact mechanism of the photochemical changes is still obscure. According to one theory a subhalide, *e.g.* Ag_2Br, is formed by the transfer of bromine to the sensitizer. Scheele's original experiments prove that chemical reactions occur when the action of light is prolonged, and loss of chlorine with the formation of silver (not subhalide) has been established by experiments with the microbalance (Hartung, *J.C.S.*, 1922, **121**, 682 ; 1924, **125**, 2198 ; 1925, **127**, 2691). Up to 95 p.c. may be decomposed. Rehalogenation restores the original weight and colour. Other work points to a physical explanation (Joly, 1905). Halides of silver on exposure to light emit electrons, and the photo-sensitiveness is in the order of the photo-electric effect : AgBr > AgCl > AgI. Cathode rays (free electrons) and X-rays (which produce free electrons from matter) also produce photographic effects. Toy and Harrison (1928) found that the electrical conductivity of silver halides increases on exposure to light, and suggest that the halogen ions lose the extra electron, which converts a silver ion to a silver atom. The quantum efficiency is 1 (Eggert and Noddack, 1923) : the primary process is confined to the halide ion : $Hal' = Hal + \ominus$, followed by the secondary reaction $Ag^{\cdot} + \ominus = Ag$. According to Hamburger (1933) as few as three silver atoms arranged as in the silver crystal lattice are able to act as a centre from which development may proceed. It seems to be well established that photosensitivity depends to some extent on the nature of the adsorbed gelatin-silver or dye-silver complex on the surface of the halide crystals.

Gold

Gold ornaments are found in neolithic remains in all the earliest centres of civilisation (Egypt, Babylonia, etc.) and the metal was obtained both from alluvial deposits and from rocks by crushing, washing and refining.

Gold usually occurs native, alloyed with silver and copper and sometimes traces of platinum. Some tellurium compounds of gold occur in small amounts, and traces of gold are found in pyrites and other ores. It occurs in sea water (0·01–0·05 mg. per cu. m.), mostly as suspended metal (Haber, 1927).

Native gold occurs either in alluvial deposits or in veins in quartz intersecting metamorphic rocks, and also in many other formations, *e.g.* the Lower Silurian in Wales, and even up to the chalk. The most important European sources are the Urals and Hungary. Hungarian gold may contain tellurium, which must be removed. The richest fields are in Africa, especially the Transvaal. In North America the fields extend from Mexico to Klondike. Australian gold often contains silver and is pale in colour. *Electrum* is a native alloy of gold and 15–45 p.c. of silver; *green gold* contains 10 p.c. of silver: these alloys were called *asem* in ancient Egypt.

Native gold occurs as nuggets or as grains in alluvial sand or gravel, from which it is extracted by washing in agitating cradles or sluices, or by breaking up the gravel by powerful jets of water. Gold-bearing rock is crushed in stamps or ball mills. By modern processes quartz with 0·001 p.c. and gravel with 0·0003 p.c. of gold can be worked. In working gravel the grains of gold are separated by passing the mud through long wooden troughs with battens across the bottom, or over blankets. The slime from mills is sometimes passed over amalgamated copper plates: gold is only slightly soluble in mercury and the separation is due to adhesion. The amalgam is scraped off and distilled in iron retorts, and the residue cupelled.

Auriferous pyrites or "concentrates" are treated by Percy and Plattner's **chlorine process** (1846). They are roasted, moistened, and exposed to chlorine gas in tubs with false bottoms. After 24 hours the soluble gold chloride $AuCl_3$ is leached out with water and the gold precipitated with ferrous sulphate: $AuCl_3 + 3FeSO_4 = Au + FeCl_3 + Fe_2(SO_4)_3$, or with hydrogen sulphide or charcoal. Bromine water may be used instead of chlorine, and cyanogen bromide is used in Australia with gold containing tellurium, which is not attacked by cyanide.

Gold is extracted directly from the finely stamped rock or the "tailings" of other processes by the **cyanide process** (MacArthur and Forrest, 1887). The ore is percolated or the slimes agitated in large tanks with cyanide solution containing the equivalent of 0·1 p.c. of KCN, usually made alkaline by lime, in which the gold dissolves. After settling or filter-pressing the clear liquid is reduced by charcoal or metallic zinc (used in packing the cyanide). The precipitate is fused in plumbago crucibles and the gold refined.

The reaction in the cyanide process forms the aurocyanide ion $Au(CN)_2'$ (Elsner, 1846; MacLaurin, *J.C.S.*, 1893, **63**, 724; 1895, **67**, 199):

$$4Au + 8CN' + 2H_2O + O_2 = 4Au(CN)_2' + 4OH',$$

probably with the intermediate formation of hydrogen peroxide (Bodländer, 1896):

$$2Au + 4CN' + 2H_2O + O_2 = 2Au(CN)_2' + 2OH' + H_2O_2$$
$$2Au + 4CN' + H_2O_2 \quad\quad = 2Au(CN)_2' + 2OH'.$$

The precipitation with zinc :

$$2Au(CN)_2' + Zn = Zn(CN)_4'' + 2Au$$

is accompanied by some evolution of hydrogen :

$$Zn + 4CN' + 2H_2O = Zn(CN)_4'' + 2OH' + H_2.$$

If the gold bullion contains copper this is removed by oxidising fusion with borax and nitre. Silver and gold are separated by boiling the granulated alloy in cast-iron pots with concentrated sulphuric acid, which dissolves the silver as sulphate (Scheffer, 1753).

The alloy must not contain more than one-third of gold, otherwise the silver is not dissolved. If it contains more it is melted with silver until it contains one-quarter its weight of gold, hence the process is termed *quartation.* Parting with boiling nitric acid, in which silver is dissolved from alloy containing not less than 1 part of silver to 2 of gold, is an older process still used. It was used in Venice in the fifteenth century to separate gold from Spanish silver.

In the *electrolytic process* of Wohlwill (*J.S.C.I.*, 1898, **17**, 585) the gold bullion is made the anode in 2·5–6 p.c. gold chloride solution containing 2–5 p.c. of hydrochloric acid, and an alternating current is superposed on the direct current. In the **Rose process** (1910) the zinc precipitates are fused and air or oxygen blown through, when base metals oxidise and pass into a borax-silica flux. In **Miller's process** (1869), used at Ottawa Mint, chlorine gas is passed through the molten metal covered with borax, when silver chloride is formed and floats to the top.

Pure gold is too soft for ornaments or coinage and is alloyed with copper or silver or both. The copper makes the colour redder, silver makes it pale.

The *fineness* is expressed in *carats*, pure gold being 24 carat, and five standard alloys of 22, 18, 15, 12, and 9 carat, *i.e.* parts of gold in 24 of alloy, are legalised. One part of bismuth in 1920 parts of gold or 1 part of lead in 1000 of gold makes the metal brittle. Gold forms a purple alloy $AuAl_2$ with aluminium.

Gold plating is carried out by electro-deposition from solutions in potassium cyanide, the requisite amounts of silver and copper salts being added. These metals deposit with the gold if a suitable voltage is used.

Properties of gold.—Gold is bright yellow, rather soft, crystallises (like most metals) in the cubic system, has a high s.g. of 19·3 and is a good conductor of heat and electricity. It melts at 1063°, expanding on fusion, to a bluish-green liquid, volatilises appreciably 100° above its melting point and boils at 2610°. Molten gold does not dissolve oxygen. Gold is the most ductile metal and can be beaten into leaves 0·00009 mm. thick. Ordinary leaf is 0·0001 mm., gold on gold lace 0·000002 mm., thick. Gold leaf transmits green light. On heating at 316° it transmits red light ; at 550° it crystallises and minute gaps are formed which make it seem transparent. Films less than 10^{-5} mm. thick have been obtained (G. P. Thomson, *Proc. Roy. Soc.*, 1929, **125**, 352). Gold is not attacked by oxygen or any single acid except selenic, but dissolves in solutions of chlorine, bromine or iodine, and therefore in aqua regia (1 part conc. HNO_3

+4 parts conc. HCl). Fused alkalis and nitrates or sodium peroxide, a solution of ferric bromide, telluric acid with sulphuric acid, iodic and periodic acids in hot sulphuric acid, and some other oxidising reagents, also attack it. Gold differs from copper and to some extent from silver in the extreme ease with which its compounds are reduced to the metal.

Colloidal gold is formed by Bredig's process (p. 86), or by reducing solutions of gold chloride with phosphorus (Faraday, *Phil. Trans.*, 1857, **147**, 145), hydrazine, formaldehyde, etc. The solutions have different colours according to the nature of the colloidal particles. Those with coarse particles are blue; with increasing fineness the colour passes to a fine ruby-red. According to Ambronn, Siedentopf, and Zsigmondy, the colour depends also on the shape of the particles; the particles are crystalline, the smallest having only 5 atoms in a side of the cube.

By precipitating gold chloride with stannous chloride, a purple powder called *purple of Cassius* (discovered by Andreas Cassius and described by Orschall in 1684 and by Cassius' son in 1685), used for making ruby glass, is deposited. It appears to be colloidal stannic oxide with adsorbed colloidal gold (Faraday, 1857; Moissan, 1905):

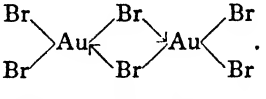
$$2AuCl_3 + 3SnCl_2 + 6H_2O = 2Au + 3SnO_2 + 12HCl.$$

Similar purples are formed by precipitating gold on hydroxides of magnesium, aluminium and antimony by reducing in alkaline solution with grape-sugar. Zsigmondy (1898) prepared purple of Cassius by mixing colloidal gold and colloidal stannic oxide and precipitating with an acid or salt. The X-ray spectrum shows the lines of gold and stannic oxide (Huber, 1924).

When glass is fused with purple of Cassius it is colourless, but when annealed it assumes a fine ruby colour, due to the presence of ultramicroscopic particles of gold.

Gold Compounds

Gold forms **aurous compounds** AuX, all sparingly soluble, in which it is univalent, and **auric compounds** AuX_3 in which it is tervalent; the auric compounds are more important. Compounds ($AuCl_2$, $AuBr_2$, AuO, AuS, $AuSO_4$) apparently containing bivalent gold may contain uni- and tervalent gold ($Au[AuCl_4]$, etc.). Gold shows a marked tendency to covalency with a coordination number of 4 in auric compounds (Gibson, etc., *J.C.S.*, 1930 f.), *e.g.* gold tribromide is probably:



The increased volatility of gold in hydrogen at 1400° has been attributed to the formation of a **hydride** AuH (Farkas, 1929), and the action of atomic hydrogen on gold foil forms a white powder, decomposing above 100° and turned brown by sodium hydroxide and by hydrogen sulphide owing to the formation of gold hydroxide and sulphide (Pietsch and Josephy, 1931).

Gold dissolves in aqua regia to a bright yellow solution which on evaporation deposits deliquescent yellow crystals of **chlorauric acid** $HAuCl_4,3$ or $4H_2O$, soluble in water, alcohol and ether. These lose hydrogen chloride at 120° to form deep red crystalline **auric chloride** $AuCl_3$, which is also formed on evaporating a solution of gold in chlorine water and heating at 150°.

Chlorauric acid (commonly called " gold chloride ") in solution is easily reduced to gold by hydrogen gas or exposure to light. It forms salts, *e.g.* light yellow crystals of $KAuCl_4,\frac{1}{2}H_2O$ on mixing with concentrated hydrochloric acid and KCl.

At 175° $AuCl_3$ decomposes to a light yellow powder of **aurous chloride** AuCl, which at higher temperatures is reduced to gold. Aurous choride is insoluble but is decomposed by cold water: $3AuCl = AuCl_3 + 2Au$. It forms a carbonyl Au(CO)Cl with carbon monoxide. On heating, $KAuCl_4$ forms the aurous compound $KAuCl_2$.

Auric bromide $AuBr_3$ is formed in black crystals by dissolving gold in bromine. With hydrobromic acid it forms deep scarlet **bromauric acid** $HAuBr_4$, 5 or $6H_2O$, soluble in ether, and with potassium bromide purple-red $KAuBr_4,2H_2O$. At 115° $AuBr_3$ forms yellowish-grey or green **aurous bromide** AuBr, decomposed at a somewhat higher temperature into gold. A colourless solution of potassium bromaurite $KAuBr_2$ is formed by reducing ice-cold $KAuBr_4$ solution with sulphur dioxide solution.

A green precipitate of **auric iodide** AuI_3 is formed on adding gold chloride solution to potassium iodide solution, but it soon decomposes into aurous iodide and iodine (cf. CuI_2). It forms with hydriodic acid black crystals of $HAuI_4$ and dissolves in potassium iodide solution to form $KAuI_4$, black crystals decomposed by heat with separation of gold. **Aurous iodide** AuI is formed as a yellow or greenish-yellow crystalline powder by the action of iodine at 50°–114°, or in ether solution, on gold. It is decomposed by heat and by water only on warming. All the halides of univalent gold form several compounds with ammonia.

By the action of cold dilute alkali on aurous chloride a violet powder said to be **aurous hydroxide** AuOH is formed, which at 200° is said to form violet-grey **aurous oxide** Au_2O; according to Pollard (*J.C.S.*, 1926, 529, 1347; Hartung, *J.C.S.*, 1926, 1349; Gerke and Rourke, *J.A.C.S.*, 1927, **49**, 1855) it is a mixture of gold and auric oxide Au_2O_3. Pure aurous oxide is said to be formed as a violet powder by precipitating a solution of potassium bromaurite with dilute alkali, drying the AuOH over P_2O_5, and dehydrating at 200° (above 205° it loses oxygen). It is a very weak base.

Auric hydroxide is formed in small yield as a reddish-brown powder by decomposing gold chloride ($HAuCl_4$) solution with alkali, or better with magnesium oxide or basic carbonate, and washing with dilute nitric acid (in which most of it dissolves). It is a very weak base; it also dissolves in hot potassium hydroxide solution and on evaporation in vacuum pale yellow needles of **potassium aurate** $KAuO_2,3H_2O$ separate. Sodium aurate $NaAuO_2,H_2O$ is formed by fusing gold powder with sodium peroxide, dissolving and crystallising.

Auric hydroxide dissolves in ammonia, perhaps forming $[Au(NH_3)_4](OH)_3$. On drying over P_2O_5 the hydroxide forms Au_2O_3,H_2O or $HAuO_2$; at 140°–150°

it slowly forms **auric oxide** Au_2O_3, and at higher temperatures metallic gold. (AuO is said to be formed at 155°–165°.)

Three gold **sulphides** are described. **Aurous sulphide** Au_2S is formed as a greyish-black precipitate on saturating a solution of potassium aurocyanide with hydrogen sulphide and adding hydrochloric acid to the clear solution. It dissolves in sodium polysulphide solution forming sodium aurisulphide $NaAuS_2$ (a compound of 3-valent gold). AuS (perhaps $Au^I[Au^{III}S_2]$) is precipitated on passing hydrogen sulphide into neutral gold chloride solution: $8AuCl_3 + 9H_2S + 4H_2O = 8AuS + 24HCl + H_2SO_4$. **Auric sulphide** Au_2S_3 is formed as an amorphous black powder by the action of hydrogen sulphide at −10° on lithium chloraurate, $LiAuCl_4,2H_2O$:

$$2LiAuCl_4 + 3H_2S = Au_2S_3 + 2LiCl + 6HCl,$$

extracting the LiCl by alcohol, and drying at 70°. It is decomposed by water.

Gold when fused with sodium sulphide and sulphur forms a mass soluble in water and the solution on evaporation in vacuum deposits colourless crystals of **sodium sulphaurate** $NaAuS_2,4H_2O$ (derived from Au_2S_3). Stahl (1715) fancifully suggested that Moses used this method to dissolve the Golden Calf!

The complex **sodium aurothiosulphate** $Na_3[Au^I(S_2O_3)_2],\frac{1}{2}H_2O$ formed by the reaction: $AuCl_3 + 4Na_2S_2O_3 = Na_3[Au(S_2O_3)_2] + Na_2S_4O_6 + 3NaCl$, crystallises in colourless needles and is used in medicine as *sanochrysin* (Greek *chrusos*, gold). It is not reduced by ferrous sulphate, oxalic acid or stannous chloride.

Potassium aurocyanide $KAu(CN)_2$ is an important compound, formed when gold dissolves in potassium cyanide solution in presence of oxygen and on dissolving fulminating gold (see below) in boiling potassium cyanide solution, separating on cooling in colourless crystals. On evaporating a solution in hydrochloric acid and washing the residue yellow **aurous cyanide** AuCN remains.

Colourless crystals of **potassium auricyanide** $KAu^{III}CN)_4,\frac{3}{2}H_2O$ deposit on cooling a hot concentrated solution of auric chloride and potassium cyanide: it is not reduced by ferrous sulphate. The free acid $HAu(CN)_4,6H_2O$ (sometimes described as auric cyanide, $Au(CN)_3$, $\frac{3}{2}$ or $3H_2O$) is formed in colourless crystals by decomposing a solution of $KAu(CN)_4$ with H_2SiF_6 and evaporating the filtrate in vacuum over concentrated sulphuric acid. **Potassium aurothiocyanate** $KAu(CNS)_2$ crystallises in colourless needles, and the **aurithiocyanate** $KAu(CNS)_4$ is known.

Oxysalts of gold are very uncommon. Besides the **sulphates** $AuSO_4$ and $Au_2(SO_4)_3$ (probably $(AuO)HSO_4$) there is an **acid nitrate** $H[Au(NO_3)_4],3H_2O$ (which forms crystalline salts), basic nitrates, and a fairly stable yellow crystalline **selenate** $Au_2(SeO_4)_3$ separating from a solution of gold in hot selenic acid. The salt $[Au(NH_3)_4](NO_3)_3$ forms yellow crystals.

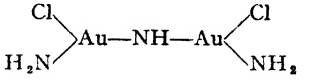
The supposed compounds of *bivalent gold* are now usually regarded as complex compounds containing univalent gold in the cation and tervalent gold in the anion, *e.g.* $AuCl_2$ is $Au^I[Au^{III}Cl_4]$, etc.

$AuCl_3$ and $AuBr_3$ were said by Thomsen (1883) to be formed as dark-coloured solids by the action of chlorine and bromine on gold powder at 170°, but their existence is doubtful. A monoxide AuO (perhaps $Au^I(Au^{III}O_2)$ or gold aurate), oxide

hydrate $Au_2O_3(OH)_3$, sulphide AuS or $Au^I[Au^{III}S_2]$, and sulphate $AuSO_4$ or $Au^I[Au^{III}(SO_4)_2]$ are described.

Fulminating gold is an olive-green powder of rather variable composition formed by digesting auric oxide or hydroxide with ammonia. When dry it detonates violently when heated or struck, forming gold, nitrogen, ammonia and steam.

Raschig (1886) formulated fulminating gold as $HN{=}Au{-}NH_2,\frac{3}{2}H_2O$. It is also precipitated by ammonia from gold chloride solution and then contains some chlorine, according to Raschig in the form HN=Au—Cl, but according to Weitz (*Annalen*, 1915, **410**, 117) this fulminating gold is



with chlorine partly replaced by OH. Its explosibility is increased on washing with ammonia, when perhaps $[Au(NH_3)_2(OH)_2]OH$ is formed. By the action of ammonia on aurous oxide **sesquiauramine** NAu_3,NH_3 is formed, which on boiling with water forms **aurous nitride** Au_3N.

CHAPTER XIV

THE ALKALINE EARTH METALS

THE elements of Group II are all metals, which are divided into two sub-groups :

(*a*) **Even series :** beryllium, magnesium, calcium, strontium, barium and radium.

(*b*) **Odd series :** zinc, cadmium and mercury.

The physical properties of elements of the **even series** (except radium) are :

	Be	Mg	Ca	Sr	Ba
Atomic number -	4	12	20	38	56
Electron configuration	2·2	2·8·2	2·8·8·2	2·8·18·8·2	2·8·18·18·8·2
Density - - -	1·84	1·74	1·55	2·54	3·78
Atomic volume -	4·90	13·97	25·9	34·5	36·7
Melting point * -	1280°	651°	851°	800°	710°
Boiling point * -	1500°	1100°	1439°	1366°	1537°

These (except beryllium) are sometimes called the metals of the *alkaline earths*. The old chemists gave the name " earth " to all non-metallic substances insoluble in water and unchanged by fire ; lime and magnesia (which are somewhat soluble) were found to have an alkaline reaction, and the other alkaline earths discovered were baryta (Scheele, 1774) and strontia (Crawford, 1790). Lavoisier suggested that the earths were probably metallic oxides, and magnesium and the alkaline earth metals were isolated by Davy in 1808. Beryllium oxide and salts were discovered by Vauquelin in 1798 and the metal by Bussy and by Wöhler in 1828 ; the question of its valency is discussed on p. 180.

The physical properties of the metals of the **odd series** are :

	Zn	Cd	Hg
Atomic number - - -	30	48	80
Electron configuration - -	2·8·18·2	2·8·18·18·2	2·8·18·32·18·2
Density - - - - -	7·1	8·64	13·5955(0°)
Atomic volume - - -	9·21	13·01	14·02
Melting point - - - -	419·4°	320·9°	− 38·90°
Boiling point - - - -	920°	767·3°	356·95°

The two parts of Group II are much more alike than those of Group I although they differ more than the odd and even series of Groups III and IV, where there is very little difference between the series in a group. Beryllium and magnesium in many ways resemble the elements of the odd series, with which they are often classified, and beryllium shows many analogies not only with magnesium but also aluminium in Group III : beryllium hydroxide is precipitated by ammonia and dissolves in sodium hydroxide solution, and beryllium salts are hydrolysed. This divergence from group properties is

* Widely discrepant figures are given for these.

probably connected with the small size of the $Be^{\cdot\cdot}$ ion: the ions $Mg^{\cdot\cdot}$, $Ca^{\cdot\cdot}$, $Sr^{\cdot\cdot}$ and $Ba^{\cdot\cdot}$ form increasingly strong basic oxides.

The normal valency in the group (probably also in the mercurous compounds Hg_2X_2) is two, although some *subhalides* are described, red Ca_2Cl_2 and Ba_2Cl_2, formed by heating the normal chlorides with the metals at 1000° and on the cathode in the electrolysis of fused halides, and *suboxides* Ca_2O and Ba_2O by heating the oxides with magnesium (Guntz, 1906).

The uniform bivalency of the metals of the even series depends on the facts that: (*a*) the second outer electron is easily removed so that both are lost together; (*b*) the resulting cation has an inert gas configuration (8 outer electrons) and hence is very stable, so that no electrovalencies higher than 2 are shown.

The electro-affinity of the elements is in the decreasing order: (Ra), Ba, Sr, Ca, Mg, Be, Zn, Cd, Hg, and the standard electrode potentials in volts at 25° are:

Be	Mg	Ca	Sr	Ba	Zn	Cd	($Hg^{\cdot\cdot}$)
−1·70	−2·34	−2·87	−2·89	−2·90	−0·762	−0·402	+0·854

All the elements form basic oxides MO (mercury also forms the basic oxide Hg_2O) and, except mercury, basic hydroxides $M(OH)_2$, the solubility of which in the even series increases with the atomic weight: $Ca(OH)_2$ 0·163, $Sr(OH)_2$ 0·81, $Ba(OH)_2$ 3·75 g./100 g. H_2O at 20°; those of Be and Mg and of the odd series elements are very sparingly soluble. Cadmium oxide is brown, mercurous oxide black and mercuric oxide yellow or red; the other oxides are white but zinc oxide is yellow when hot.

Barium oxide combines with oxygen on heating at atmospheric pressure to form a peroxide, strontium oxide only under pressure, and unstable hydrated peroxides of the other elements (except beryllium) are formed only indirectly, *e.g.* by the action of hydrogen peroxide on the oxides or hydroxides.

The metals are all silver-white. Beryllium, magnesium, zinc and cadmium crystallise in close-packed hexagonal, mercury in rhombohedral, lattices, the alkaline earth metals in cubic lattices. Calcium, strontium, barium and radium oxidise in the air and more easily the higher the atomic weight (the increasing nuclear charge is apparently largely screened by inner shells of electrons); magnesium and zinc oxidise only slowly at room temperature; beryllium, cadmium and mercury are stable in air. Calcium, strontium and barium decompose cold water, magnesium powder decomposes hot water slowly, and zinc and cadmium decompose steam on heating.

Calcium, strontium and barium form *hydrides* MH_2, and they, and also magnesium and radium, form *nitrides* M_3N_2 directly; the other metals form nitrides indirectly.

Beryllium and magnesium resemble the elements of the odd series in forming soluble *sulphates*, $BeSO_4,4H_2O$ and $MgSO_4,7H_2O$ (isomorphous with $ZnSO_4,7H_2O$), and double sulphates, $K_2Be(SO_4)_2,2H_2O$ and $K_2Mg(SO_4)_2,6H_2O$ (isomorphous with $K_2Zn(SO_4)_2,6H_2O$), and in forming organometallic com-

pounds $Be(CH_3)_2$ and $Mg(CH_3)_2$, etc., similar to $Zn(CH_3)_2$, $Cd(CH_3)_2$, $Hg(CH_3)_2$, etc. Although $CaSO_4$ is slightly soluble and forms a hydrate $CaSO_4,2H_2O$, $SrSO_4$, $BaSO_4$, and $RaSO_4$ are practically insoluble. The sulphides of beryllium, magnesium, and the alkaline earth metals are not precipitated from solution by hydrogen sulphide; those of zinc, cadmium and mercury are, and decrease in solubility in this order. The sulphides of Be, Mg, Ca, Sr and Ba are hydrolysed by water; ZnS is soluble in dilute and CdS in concentrated hydrochloric acid, whilst HgS is insoluble even in boiling nitric acid but dissolves in hot aqua regia.

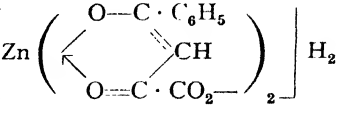
The solubilities of the chlorides, bromides, iodides, nitrates and sulphates decrease, but the solubilities of the fluorides, oxalates and hydroxides increase, from calcium to barium; the carbonates are about equally soluble. The halides of all the elements except barium dissolve in alcohol; $BeCl_2$ and $HgCl_2$ are even soluble in ether, and calcium nitrate is soluble in alcohol.

The gradation in electro-affinity is shown in the decomposition of the hydroxides and carbonates by heat; this occurs least easily with barium, and increases through strontium to calcium; those of the remaining elements are easily decomposed, mercury forming no hydroxide or normal carbonate at all. The ease of reduction of the oxides increases from zinc to mercury.

Zinc, cadmium and mercury are sometimes classed as *transitional elements* (p. 261), since the cations have 18-electron shells, although they are uniformly bivalent. They show an increasing tendency to form covalent compounds from zinc to mercury, fused zinc chloride being a conductor but mercuric halides almost non-ionised. Mercury is peculiar in forming the two series of **mercurous** and **mercuric** compounds, with entirely different reactions. The mercurous compounds closely resemble those of silver or univalent copper; the mercuric are analogous to compounds of bivalent copper, zinc and cadmium. Although mercurous compounds might seem to contain univalent mercury, their formulae are double and they contain the bivalent complex —Hg—Hg—, the ion being $Hg_2^{\cdot\cdot}$.

Beryllium, magnesium, zinc, cadmium and mercury do not give distinctive flame colorations: calcium gives an orange-red flame colour, strontium crimson, barium apple-green, and radium carmine red.

Zinc shows a covalency of 4 with a tetrahedral arrangement of valencies in the optically active derivatives of benzoylpyruvic acid (Mills and Gotts, *J.C.S.*, 1926, 3121):



and zinc and cadmium show a covalency of 6 with an octahedral arrangement of valencies in the optically active compounds with ethylenediamine (Neogi and Mukherjee, 1934): $[Zn\ en_3]Cl_2$ and $[Cd\ en_3]Cl_2$.

Beryllium

Vauquelin (1798) discovered in the mineral *beryl*, which forms hexagonal crystals (Fig. 181), a peculiar "earth," which was called *glucina*, since its salts have a sweet taste. The Peruvian *emerald* is a transparent variety of beryl coloured green by chromium oxide, *aquamarine* is a bluish-green variety. The formula of beryl is $3BeO$, Al_2O_3, $6SiO_2$. *Bromellite* BeO occurs in Sweden, *chrysoberyl* is $BeAl_2O_4$.

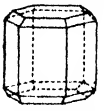


FIG. 181.—Crystal of beryl.

To prepare beryllium salts, beryl is fused with potassium carbonate, the melt evaporated with concentrated sulphuric acid, and the residue extracted with water. Silica is filtered off and on evaporating and cooling the filtrate much of the aluminium crystallises as potash alum. The liquid is poured into concentrated ammonium carbonate solution, when ferric and aluminium hydroxides precipitate. The filtrate on boiling deposits **basic beryllium carbonate** of variable composition. On ignition this gives the refractory **beryllium oxide** BeO as a white powder, m.p. 2750°.

Beryllium hydroxide $Be(OH)_2$ is soluble in alkalis but is reprecipitated on boiling. It is insoluble in ammonia, but readily soluble in ammonium carbonate, the solution depositing basic beryllium carbonate on boiling or when a rapid current of steam is passed through it. These reactions distinguish beryllium from aluminium.

By passing chlorine over a heated mixture of BeO and carbon **beryllium chloride** $BeCl_2$ sublimes in white needles, which fume strongly in moist air, m.p. 440° (the fused salt is a poor conductor of electricity), b.p. 520° (Field, *J.A.C.S.*, 1939, **61**, 1817). The vapour density above 630° corresponds with $BeCl_2$. There is a soluble **fluoride** BeF_2 and a **basic fluoride** $5BeF_2,2BeO$.

The **metal** is obtained by electrolysis of a fused mixture of beryllium and sodium chlorides, by heating the chloride with potassium, or (in the fused state) by electrolysing a fused mixture of barium fluoride and basic beryllium fluoride in a graphite vessel with a water-cooled iron cathode. It is white, hard and brittle, m.p. 1280°, s.g. 1·842. The grey powder on heating in air burns brilliantly, but it does not decompose steam at a red heat. Beryllium is readily soluble in dilute sulphuric and hydrochloric acids, but not in nitric acid, and is easily soluble in alkalis (cf. Al). The metal is used in some light alloys, and beryllium bronzes (2·5 p.c. Be) have many properties of steel and can be tempered. Thin sheets of beryllium, which (on account of the low atomic number) are transparent to X-rays, are used as windows for some X-ray tubes.

Beryllium nitrate $Be(NO_3)_2,3H_2O$, which is deliquescent and does not easily crystallise, is used in making gas mantles, a small quantity being added to the thorium and cerium nitrates.

Beryllium sulphide BeS is stable to water but is decomposed by acids, even carbonic. A solution of beryllium oxide in hot concentrated sulphuric acid deposits on cooling crystals of **beryllium sulphate**, which crystallises from water as $BeSO_4.4H_2O$, and forms double sulphates, *e.g.* $K_2Be(SO_4)_2,2H_2O$: $BeSO_4$ does not form mixed crystals with $CuSO_4$ or $FeSO_4$. Beryllium sulphate is stable up to 540°; it is hydrolysed in solution.

On evaporating beryllium hydroxide with acetic acid a covalent **basic acetate** $Be_4O(C_2H_3O_2)_6$ is formed, readily volatile (b.p. 330°) giving the normal vapour density, and soluble in chloroform. The X-rays show that the four beryllium

atoms are arranged at the corners of a regular tetrahedron with the oxygen at the centre, and the six edges occupied by acetate groups (Bragg and Morgan, *Proc. Roy. Soc.*, 1923, **104**, 437).

Magnesium

Crystals of *Epsom salt* $MgSO_4,7H_2O$ were obtained from Epsom spring water by Nehemiah Grew in 1695. The chloride $MgCl_2$ occurs in sea water. By mixing solutions of these salts with alkali carbonates a basic magnesium carbonate called *magnesia alba* is precipitated, and Black in a famous research showed in 1754 that this on heating gives off water and fixed air (CO_2) and leaves *calcined magnesia* MgO. Magnesium and calcium compounds had been distinguished by F. Hoffmann in 1722. Impure metallic magnesium was obtained by Davy in 1808.

Magnesium is widely and plentifully distributed. It occurs as *magnesite* $MgCO_3$ (large amounts in Greece) and *dolomite* $MgCO_3$, $CaCO_3$ or $MgCa(CO_3)_2$; *kieserite* $MgSO_4,H_2O$, *kainite* $KCl,MgSO_4,3H_2O$, *carnallite* $KMgCl_3,6H_2O$, and *picromerite* or *schönite* $K_2Mg(SO_4)_2,6H_2O$, are Stassfurt minerals. It occurs in rock minerals: *spinel* $MgAl_2O_4$, *talc* (or *steatite*) $Mg_3H_2(SiO_3)_4$, *forsterite* Mg_2SiO_4 (which in isomorphous mixture with fayalite Fe_2SiO_4 forms *olivine*, a gem variety of which is *peridot* or *chrysolite*), *asbestos* $CaMg_3(SiO_3)_4$, *meerschaum* $Mg_2H_2(SiO_3)_3,H_2O$, *serpentine* $Mg_3H_4Si_2O_9$ and *augite* $CaMg(SiO_3)_2$.

Plant and animal tissues contain magnesium as an essential constituent, *e.g.* of chlorophyll, the green colouring matter in plants.

Magnesium forms very few complex ions but a great number of double salts. Apart from its resemblances to zinc and cadmium, it shows some analogies with bivalent iron, cobalt, copper and manganese in its salts, in which it is always bivalent. In solution the hydrated $Mg^{\cdot\cdot}$ ion is formed.

Magnesium was obtained by Bussy (1829) by heating the anhydrous chloride with potassium, and by Bunsen (1852) by electrolysis of the fused chloride (m.p. 708°). It is made technically by electrolysis of the fused chloride (made by passing chlorine over a red-hot mixture of magnesium oxide and carbon), or of a solution of the oxide in the fused chloride by a process like that used for aluminium (p. 417), or of fused carnallite, which loses water and fuses below 700°. The cathode is the iron crucible, the carbon anode is surrounded by a perforated porcelain tube leading off the chlorine, and the metal floats to the surface in the cathode compartment, where it is protected from oxidation by a current of coal gas.

In another process a magnesium-lead alloy is made by electrolysing fused magnesium and potassium chlorides with a carbon anode and a fused lead cathode, and the alloy is then fused in another cell with the same electrolyte but made the anode, the magnesium being deposited on cathodes of steel rods. An electrothermic method of reduction of the oxide with carbon at 2000° is also used: the vapour is rapidly chilled by hydrogen at 200° as the reaction is reversible: $MgO + C \rightleftharpoons Mg + CO$.

The semi-fused metal is pressed into wire which is rolled into ribbon. Magnesium is silver-white and soft, of low s.g. 1·74, and m.p. 651°, b.p. 1100°.

It is ductile at 450°. Fine hexagonal crystals are formed by subliming in vacuum at about 550°, and the metal may be purified in this way. Magnesium is a constituent of many light alloys, *e.g.* with zinc and aluminium, and is also used in deoxidising fused brass, bronze, and nickel. It burns with an intense white light when heated in air, and also burns when heated in chlorine (unless quite dry), and in bromine and iodine vapours; it combines on heating with carbon, silicon, nitrogen, phosphorus and arsenic, and continues to burn in sulphur vapour, steam, carbon dioxide, sulphur dioxide, nitric oxide and nitrogen dioxide.

Heated magnesium reduces carbon monoxide, oxides of most metals (including those of calcium, strontium and barium), alkali hydroxides and carbonates, and many metallic salts. Magnesium powder mixed with powdered potassium chlorate or barium peroxide burns explosively with a blinding white flash and the mixture is used in photography and for signalling and star-shells. A mixture of magnesium and dry amorphous silica may also be used. (Aluminium powder or a mixture of it with magnesium powder is now often used, or aluminium foil in a bulb of oxygen at low pressure is ignited by a low-voltage filament.) The metal is stable in dry air, but soon becomes covered with oxide in moist air: the alloys with lead, containing Mg_2Pb, rapidly oxidise in air.

Amalgamated magnesium decomposes cold water and magnesium powder hot water, with evolution of hydrogen. The metal dissolves readily in dilute acids but not in alkalis. It reacts with many salt solutions (Getman, *J.A.C.S.*, 1917, **39**, 596), *e.g.* with hot ferric chloride solution:

$$3Mg + 2FeCl_3 + 6H_2O = 3MgCl_2 + 2Fe(OH)_3 + 3H_2,$$

and deposits more electropositive metals such as silver, lead, mercury and copper, although the reaction is rarely quantitative, some hydrogen being evolved and basic salts precipitated; some cuprous oxide is formed with copper sulphate solution (see p. 330). A colloidal solution of magnesium in ether is green.

Magnesium Compounds

Magnesium oxide (*magnesia*) MgO occurs sparingly in octahedral crystals as *periclase*, an artificial form of which is used as a heat insulator. Magnesium oxide is prepared by heating the nitrate or basic carbonate or native magnesite, and is called *calcined magnesia*. A light and a heavy form, with densities in the ratio 1 : 3·5, are obtained from the light and heavy basic carbonates; the crystalline forms are the same. Magnesium oxide is refractory, m.p. 2800°, b.p. 2850°; it is reduced to carbide by carbon in the electric furnace. Crystals are formed by heating the powder strongly in a current of hydrogen chloride. Magnesium oxide slowly forms the hydroxide with water and turns moist red litmus paper blue. It slowly absorbs atmospheric moisture and carbon dioxide.

Magnesia prepared by calcining native magnesite is used to make *basic refractory bricks* for furnace-linings. These resist the action of basic slags containing lime. *Acidic* linings are composed of ganister (largely silica), and *neutral*

linings of chromite (chrome-ironstone). Bricks containing 90 parts of MgO, 5 of FeO, and 5 of silica, lime and alumina, sinter above 1400°, but do not fuse below 2000°.

Magnesium hydroxide $Mg(OH)_2$ occurs crystalline as *brucite*, which has a hexagonal layer lattice like cadmium iodide (p. 246). It is precipitated by alkali hydroxide from the chloride or sulphate solution and is insoluble in excess of alkali: it is washed and dried at 100°. It loses water above 350° (Gill, *Canad. J. Res.*, 1934, **10**, 703). It is sparingly soluble (0·01 g./lit. at 18°: Kohlrausch and Rose, 1894); the solubility is reduced by sodium or potassium hydroxide but increased by ammonium salts, especially the chloride.

The solubility in ammonium salts is probably due to the removal of OH' ions from the saturated solution of $Mg(OH)_2$ by ammonium ions:

$$NH_4^{\cdot} + OH' \rightleftharpoons NH_3 + H_2O.$$

More magnesium hydroxide can dissolve until the solubility product $[Mg^{\cdot\cdot}][OH']^2$ is reached, or, if not, until all the solid dissolves. Magnesium salts are incompletely precipitated by ammonia and not at all in presence of ammonium chloride: this is due to the small concentration of OH' ions.

Magnesium hydroxide is a strong base (it slowly absorbs carbon dioxide from the air) and magnesium salts are scarcely hydrolysed. Magnesium hydroxide forms an insoluble saccharate with cane sugar and is used in one process for sugar extraction from molasses (p. 380).

An impure hydrated **peroxide**, probably MgO_2, is obtained by precipitating with sodium hydroxide a solution of th sulphate mixed with hydrogen peroxide. After drying it contains about 8 p.c. of available oxygen and is used as an antiseptic in tooth-pastes, etc.

A black **suboxide** is said to be formed on a magnesium anode in electrolysis or by the action of magnesium on solutions of sodium or other chlorides.

Magnesium halides are:

MgF_2, tetragonal, m.p. 1396°, b.p. 2239°.	$MgCl_2$, hexagonal, m.p. 708°, b.p. 1412°.
$MgBr_2$, hexagonal, m.p. 700°.	MgI_2, hexagonal, decomp. above 700°.

The common hydrates are $MgCl_2,6H_2O$, $MgBr_2,6H_2O$ (both monoclinic) and $MgI_2,8H_2O$ ($MgI_2,6H_2O$ is stable above 44°).

Magnesium chloride $MgCl_2$ is obtained anhydrous by heating magnesium in chlorine, or a mixture of magnesium oxide and carbon in chlorine or a mixture of chlorine and carbonyl chloride. The very deliquescent hydrate $MgCl_2,6H_2O$ loses water in vacuum at 175°, but above 180° it is hydrolysed and an oxychloride is formed. The anhydrous chloride is also formed when the hydrate is heated in a stream of hydrogen chloride, or the double salt $NH_4MgCl_3,6H_2O$ is heated in a platinum dish inside a large covered clay crucible, when it first loses water and the NH_4MgCl_3 then loses ammonium chloride, leaving fused $MgCl_2$.

Magnesium chloride hexahydrate can be made by fusing carnallite $KMgCl_3,6H_2O$ at 176°, when potassium chloride deposits. On cooling, the

rest of the potassium chloride first deposits as carnallite, then the $MgCl_2,6H_2O$ crystallises. It is used in lubricating cotton threads in spinning. Magnesium chloride forms hydrates with 12 (α and β), 6, 4 and $2H_2O$.

The **oxychloride** is usually formulated as Mg_2OCl_2: when strongly heated in air it evolves chlorine (the basis of the old *Weldon-Pechiney chlorine process*): $2Mg_2OCl_2 + O_2 = 4MgO + 2Cl_2$. The only oxychloride shown on the phase diagram at 30° is $MgCl_2,3MgO,10$ or $11H_2O$ (Bury and Davies, *J.C.S.*, 1932, 2008), but the formula $MgCl_2,5MgO,17H_2O$ (Bender, 1871; Lukens, *J.A.C.S.*, 1932, **54**, 2372) is given to *Sorel's cement*, a hard white mass formed from magnesium oxide and a concentrated solution of magnesium chloride. It is used as a dental stopping and a finish for plaster, as it can be polished.

Magnesium perchlorate $Mg(ClO_4)_2$ is as good a dehydrating agent as phosphorus pentoxide (Smith, etc., *J.A.C.S.*, 1922, **44**, 2255; *Ind. Eng. Chem.*, 1924, **16**, 20).

Magnesium fluoride MgF_2 is sparingly soluble. The **bromide** $MgBr_2,6H_2O$ and **iodide** $MgI_2,8H_2O$ are similar to the chloride: they occur in some mineral springs and are formed by dissolving the oxide or carbonate in the acids.

Magnesium carbonate.—The *normal carbonate* $MgCO_3$ occurs as *magnesite*, isomorphous with calcite; the hydrate $MgCO_3,3H_2O$ (rhombic) occurs rarely as *nesquehonite*, and also crystallises after three days from a solution of 20 g. of Epsom salt and 14 g. of sodium bicarbonate in 150 c.c. of water. The solubility is 0·84 g./lit. as $MgCO_3$ at 15°; massive magnesite is very sparingly soluble, but by long contact (*e.g.* in natural water) this value may be reached. The solubility decreases with rise of temperature and is very small at 100°.

The precipitates formed by alkali carbonates and magnesium salt solutions are *basic carbonates*. At the ordinary temperature the precipitate, after drying, is a light loose powder (*magnesia alba levis*). From a boiling saturated solution a denser form is precipitated and after evaporation to dryness, washing, and drying at 100° is *magnesia alba ponderosa*. Both forms have the *approximate* formula $MgCO_3,Mg(OH)_2$ with $3\frac{1}{2}$ and $3H_2O$, respectively (Anderson, *J.C.S.*, 1905, **87**, 257; Davis, *J.S.C.I.*, 1906, **25**, 788, 973). X-ray spectra indicate the compound $5MgO,4CO_2$ with 5 or $6H_2O$ (Menzel and Brückner, 1930).

When the basic carbonate is suspended in water and carbon dioxide passed in, it dissolves, forming *fluid magnesia*. The formation of a bicarbonate is doubtful (Treadwell and Reuter, 1898). The solution at 50° deposits $MgCO_3,3H_2O$.

Magnesium carbonate which " sets " with water is formed by heating magnesium ammonium carbonate $(NH_4)_2Mg(CO_3)_2,4H_2O$ in air at 130°.

The decomposition temperature ($pCO_2 = 1$ atm.) of magnesium carbonate is variously given as 230° to 680°, but it is certainly lower than that of calcium carbonate (cf. Marc and Simek, *Z. anorg. Chem.*, 1913, **82**, 17).

Magnesium silicide Mg_2Si is formed as a steel-blue crystalline (cubic) powder by heating powdered quartz and magnesium powder in hydrogen and washing with ethyl bromide and anhydrous ether (Schwarz and Konrad, 1922).

Magnesium nitride Mg_3N_2 (cubic) is yellow when pure, and is best made by heating magnesium powder to redness in a stainless steel boat in a current of pure nitrogen in a hard glass tube (Hart and Partington, *J.C.S.*, 1943, 104); it is also formed by heating the metal in ammonia gas. It gives ammonia with water.

Magnesium nitrate $Mg(NO_3)_2,6H_2O$ crystallises in monoclinic prisms from a solution of the oxide or carbonate in dilute nitric acid. It is deliquescent and also soluble in alcohol.

Magnesium phosphide Mg_3P_2 is obtained by heating magnesium with phosphorus or a phosphate; it evolves phosphine with water. Normal **magnesium phosphate** $Mg_3(PO_4)_2$ occurs in bones and in cereal seeds and is precipitated from a solution of 20 g. of $MgSO_4,7H_2O$ in a litre of water by a solution of 19·4 g. of $Na_2HPO_4,12H_2O$ and 4 g. of $NaHCO_3$ in a litre of water. **Magnesium hydrogen phosphate** $MgHPO_4,3H_2O$ crystallises slowly from a solution of magnesium sulphate and Na_2HPO_4. With hot concentrated phosphoric acid magnesia gives **magnesium dihydrogen phosphate** $Mg(H_2PO_4)_2,2H_2O$.

Magnesium ammonium phosphate $MgNH_4PO_4,6H_2O$ occurs in some urinary calculi and deposits as a crystalline (rhombic) precipitate from solutions of a magnesium salt, ammonium chloride, ammonia and an alkali phosphate on stirring or shaking in a stoppered bottle at room temperature (cf. Balarew, *Z. anorg. Chem.*, 1918, **103**, 73). It is sparingly soluble in water (0·07 g./lit. at 15°) and less soluble in dilute ammonia (0·023 g./lit. at 15° in 1 vol. conc. ammonia + 1 vol. water). On heating to dull redness it forms **magnesium pyrophosphate** $Mg_2P_2O_7$: $2NH_4MgPO_4 = Mg_2P_2O_7 + 2NH_3 + H_2O$. The arsenate behaves similarly.

Magnesium sulphide MgS is formed by direct combination or by passing nitrogen and carbon disulphide vapour over the strongly heated sulphate or oxide. When purified by heating with a mixture of ether and ethyl iodide and a little iodine it is a reddish-white powder, not phosphorescent unless it contains traces of heavy metals (Tiede, 1916, 1922). Only the oxide is formed by heating magnesium sulphate with hydrogen or carbon:

$$2MgSO_4 + C = 2MgO + CO_2 + 2SO_2.$$

Magnesium sulphide is soluble and hydrolysed:

$$2MgS + 2H_2O = Mg(HS)_2 + Mg(OH)_2.$$

No polysulphides are known (cf. Ca and Zn). A solution of **magnesium hydrosulphide** formed by passing hydrogen sulphide into a suspension of magnesia evolves hydrogen sulphide on heating (p. 694).

Magnesium sulphate $MgSO_4$ is the most important salt. It is prepared in the laboratory by dissolving the oxide or basic carbonate in dilute sulphuric acid and evaporating, and on the large scale by boiling magnesite or dolomite with dilute sulphuric acid, filtering from calcium sulphate if dolomite is used. Iron is separated by boiling with a little precipitated magnesium carbonate and the filtrate on evaporation and cooling yields colourless rhombic crystals (Fig. 123) of *Epsom salt* $MgSO_4,7H_2O$, also formed by dissolving kieserite

($MgSO_4,H_2O$) in boiling water (it is practically insoluble in *cold* water) and crystallising, or by allowing damp kieserite to stand. Epsom salt is used as a purgative, for dressing cotton goods, and in dyeing.

Several hydrates of $MgSO_4$ are known: with 7 (2 forms, rhombic and monoclinic), 6 (2 forms (?)), 5, 4, 2 (?), $1\frac{1}{2}$, $1\frac{1}{4}$ and $1H_2O$ (Robson, *J.A.C.S.*, 1927, **49**, 2772): the anhydrous salt is formed at 200°, and when this is strongly heated in air the oxide is formed. The common hydrate $MgSO_4,7H_2O$ is isomorphous with $ZnSO_4,7H_2O$. Double salts, *e.g.* $K_2Mg(SO_4)_2,6H_2O$ (*schönite*), are readily formed with alkali-metal sulphates. A solution of magnesium sulphate in sulphuric acid deposits crystals of the *acid sulphates* $MgH_2(SO_4)_2$ and $MgH_6(SO_4)_4$.

The solubilities in g. $MgSO_4$/100 g. H_2O are:

10°	20°	30°	40°	50°	60°	70°	80°	90°	100°
31·5	36·2	40·9	45·6	50·3	55	59·6	64·2	68·9	73·8
$MgSO_4,7H_2O$				$MgSO_4,6H_2O$		$MgSO_4,H_2O$			

Above 110° the solubility decreases with rise of temperature.

Calcium

Calcium occurs widely and abundantly in many rocks as carbonate, phosphate, silicate and fluoride; in most natural waters as bicarbonate, sulphate and other salts; in plants (especially the leaves) as phosphate, etc.; in the bones of animals as phosphate, and in shells of molluscs and birds' eggs as carbonate. It forms, however, only 3·2 p.c. of the outer part of the earth (crust and sea) and is less abundant than aluminium (7·3 p.c.) and iron (4·1 p.c.). The metal was discovered by Davy in 1808.

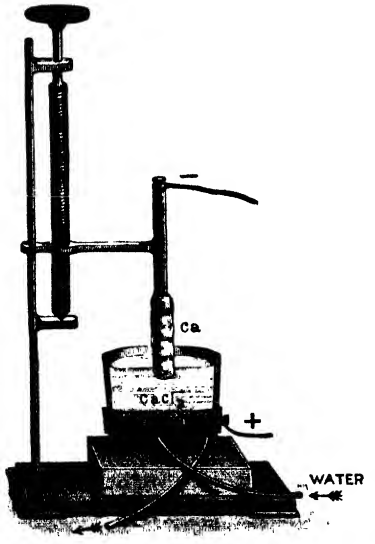


FIG. 182.—Calcium by electrolysis.

Calcium is made by the electrolysis of fused calcium chloride at 800° in a bath of carbon blocks which forms the anode. The cathode is an iron rod originally touching the surface of the fused chloride; it is slowly raised and an irregular rod of solid calcium, 20–30 cm. diam., is drawn up, protected from oxidation by a layer of chloride (Fig. 182).

Calcium is a silver-white, malleable, light metal (s. g. 1·55), rather harder than lead, m.p. 851°, and can be sublimed in vacuum below 800°. It oxidises slowly in moist air and slowly decomposes cold water. When heated it burns (forming CaO) in air and in oxygen with an intense white light, and combines

with hydrogen (forming CaH_2), nitrogen (forming Ca_3N_2), chlorine and sulphur. It reduces most metallic oxides on heating, also the chlorides and fluorides (but not iodides) of alkali metals, and many metallic salts. When rapidly heated in carbon dioxide it forms calcium oxide and carbide. Ammonia gas reacts at room temperature to form $Ca(NH_3)_6$ with evolution of heat; on heating in ammonia it reacts with incandescence, forming hydride and amide $Ca(NH_2)_2$.

Calcium removes residual oxygen and nitrogen from a vacuous space on heating (Soddy, *Proc. Roy. Soc.*, 1906, **78**, 429). It is used in hardening lead, debismuthising lead (Betterton process), deoxidising copper, iron and steel, as an alloy with aluminium, in desulphurising petroleum, and in reducing oxides of beryllium, thorium, chromium and uranium.

Calcium Compounds

Calcium hydride CaH_2 is formed with incandescence as a fused mass, stable in air, by passing hydrogen over calcium at 400°–500°. It decomposes cold water with evolution of hydrogen: $CaH_2 + 2H_2O = Ca(OH)_2 + 2H_2$.

Calcium oxide CaO (*quicklime*) is formed by heating calcium carbonate to redness: $CaCO_3 \rightleftharpoons CaO + CO_2 - 42{\cdot}5$ k. cal. If the carbon dioxide is removed by a stream of air the reaction is practically complete ("lime-burning"). The dissociation pressure increases rapidly with temperature (Smyth and Adams, *J.A.C.S.*, 1923, **45**, 1167; Southard and Royster, *J. Phys. Chem.*, 1936, **40**, 435):

$t°$ C.	- 500	600	650	700	750	800	850	897	950
p mm.	- 0·073	1·84	6·90	22·2	63·2	167	372	760	1577

$$\log p = -11355/T - 5{\cdot}388 \log T + 29{\cdot}119.$$

In *lime-burning* the limestone may be mixed with fuel in alternate layers, or the fuel may be burnt in a separate fireplace, or producer gas firing may be used. The temperature is about 1000°. Large rotary furnaces fired with powdered coal, oil, or producer gas, are used, but give a powdery product. When made from pure limestone the quicklime is nearly pure (Buxton lime is 98 p.c. CaO). Pure calcium oxide is made by heating Iceland spar in a platinum crucible with the blowpipe with free access to air until a little of the cooled product does not effervesce with acid. It is a white amorphous solid, s.g. 3·3, m.p. 2570°, b.p. 2850°; it readily sublimes in an arc furnace and condenses in cubic crystals. It merely sinters in the oxyhydrogen blowpipe flame.

Quicklime reacts with chlorine above 300°: $2CaO + 2Cl_2 = 2CaCl_2 + O_2$, and with sulphur on heating: $4CaO + 4S = 3CaS + CaSO_4$; it reacts with dry carbon dioxide only above 300° and not at all with the very dry gas (Veley, *J.S.C.*, 1893, **63**, 821; 1899, **65**, 1). It does not react in the cold with hydrogen sulphide, sulphur dioxide and nitrogen dioxide, and only slowly with hydrogen chloride.

Calcium hydroxide.—When quicklime is wetted with water it cracks, evolves steam with the evolution of much heat, and falls to a fine white powder of calcium hydroxide $Ca(OH)_2$ or *slaked lime*, s.g. 2·1: $CaO + H_2O = Ca(OH)_2 + 15{\cdot}5$ k. cal. This forms *milk of lime* when shaken with water; the decanted

clear liquid is *lime water*. The solubility is small and (as Dalton found) decreases with rise of temperature : 1·29 g. CaO at 15°, 0·67 g. at 80°, per lit.

Calcium hydroxide is formed as a white precipitate by adding alkali hydroxide solution to concentrated calcium chloride : $CaCl_2 + 2NaOH = Ca(OH)_2 + 2NaCl$. With saturated solutions the mixture becomes solid (" the chemical miracle " of Francesco Lana, 1686). Hexagonal crystals deposit on evaporating lime water in vacuum over sulphuric acid. Slaked lime heated to dull redness is converted into quicklime : $Ca(OH)_2 \rightleftharpoons CaO + H_2O$. The dissociation pressures are 100 mm. at 350° and 760 mm. at 450°. A hydrate $Ca(OH)_2,H_2O$ is described.

Quicklime exposed to the air slowly absorbs moisture and carbon dioxide, crumbling to a powder of hydroxide and carbonate, and lime water is covered with a crust of calcium carbonate.

Lime is used in chemical industries, gas purification, paper-making, tanning, making sand-lime bricks, as a fertiliser and in making lime mortar, a thick paste of slaked lime and 2–4 times as much sand (Meade, *Ind. Eng. Chem.* 1918, **10**, 214 ; Dibdin, *Trans. Faraday Soc.*, 1919, **14**, 31). A " fat " lime gives a paste with water, a " poor " lime from magnesian limestone does not.

The hardening of lime mortar consists in the evaporation of the moisture or its absorption by the bricks, and the *slow* conversion of the hydroxide into calcium carbonate by atmospheric carbon dioxide ; no combination between the lime and the silica of the sand occurs, these substances reacting at an appreciable rate only above 620° (Hüttig and Rosencranz, 1929).

Soda lime, made by slaking quicklime with sodium hydroxide solution, absorbs many gases (CO_2, SO_2, H_2S, HCl, $COCl_2$, etc.) and, as it is less fusible, is used in reactions (*e.g.* the preparation of methane) instead of sodium hydroxide.

A hydrate of **calcium peroxide** $CaO_2,8H_2O$ is precipitated in tetragonal crystals by hydrogen peroxide from lime water (Thenard, 1818) or by sodium peroxide from calcium chloride solution. It becomes anhydrous at 100°–130° and is precipitated anhydrous above 40° (Riesenfeld and Nottebohm, 1914). It is not formed directly from CaO and oxygen. The crude hydrate is made for use as an antiseptic by compressing slaked lime and sodium peroxide and washing with ice-water.

Yellow **calcium tetroxide** CaO_4, stable at 130°, is formed on warming $CaO_2,8H_2O$ alone, or better with 30 p.c. hydrogen peroxide. It evolves oxygen with dilute acids : $CaO_4 + 2HCl = CaCl_2 + O_2 + H_2O_2$, and does not liberate iodine from potassium iodide (Traube and Schulze, 1921).

Calcium Halides

CaF_2, cubic, m.p. 1330°	$CaCl_2$, rhombic, m.p. 773°, b.p. >1600°
$CaBr_2$ m.p. 730°, b.p. 810°	CaI_2, hexagonal, m.p. 740°

Hydrates : $CaCl_2$ with 6, 4 (2 forms), 2 and 1 H_2O ; $CaBr_2$ and CaI_2 with $6H_2O$ (others are reported and crystalline calcium iodide has also been formulated as $CaI_2,8H_2O$).

Ammines : $CaCl_2$ with 8, 4 and $2NH_3$ (not with $6NH_3$ as often stated) ; $CaBr_2$ with 6, 2 and $1NH_3$; CaI_2 with 8, 6, 2 and $1NH_3$.

Calcium fluoride (p. 764) is exceptional in being sparingly soluble (0·015 g./lit. at 18°); it is soluble in acids, ammonia and ammonium salts. When heated with the blowpipe on charcoal it evolves hydrofluoric acid and leaves calcium oxide. A red **subfluoride** Ca_2F_2 is said to be formed on heating CaF_2 with calcium above 1400° (Wöhler and Rodewald, 1909).

Calcium chloride is formed on dissolving lime or calcium carbonate in hydrochloric acid. On evaporating to a syrup and cooling, colourless very deliquescent hexagonal crystals of $CaCl_2,6H_2O$ separate. These dissolve in water with lowering of temperature. At 200° a white porous mass of $CaCl_2,2H_2O$ is formed, used in making solutions for refrigerators (the eutectic point is −55°): large quantities are made as a by-product in the ammonia-soda process (p. 307). On strong heating a porous mass of anhydrous $CaCl_2$ is formed, used in drying gases (it absorbs ammonia, forming $CaCl_2,8NH_3$). This melts at 773° and on cooling gives a hard crystalline mass, containing a little free lime or basic salt (from hydrolysis) unless fused in hydrogen chloride gas. The dihydrate and anhydrous salt evolve heat on dissolving in water. Calcium chloride is soluble in alcohol. Calcium chloride forms double salts, *e.g.* $KCaCl_3$.

Homberg (1693) found that freshly-fused calcium chloride is phosphorescent; Baldwin (1674) noticed the same property with calcium nitrate. Perfectly pure salts are not phosphorescent; the property is due to the presence of traces of heavy metals, such as bismuth.

Basic calcium chlorides, *e.g.* $CaCl_2,3CaO,16$ or $17H_2O$ (O'Connor, *J.C.S.*, 1927, 2700; Nikolaev and Glinskich, 1934) and $CaCl_2,CaO,2H_2O$ are described. Needles of a basic chloride separate on cooling a hot solution of calcium hydroxide in calcium chloride; they are decomposed by water.

Calcium bromide and **iodide** are prepared similarly to the chloride and are white deliquescent salts, and a double calcium silver iodide $CaI_2,2AgI,6H_2O$ is crystalline (Simpson, 1878). A red **subchloride** Ca_2Cl_2 and **subiodide** Ca_2I_2 are formed on heating the chloride and iodide with calcium and rapid cooling (Wöhler and Rodewald, 1909). A tetraiodide CaI_4 is, apparently, formed by fusing CaI_2 and iodine, and in solution.

Calcium carbide CaC_2 was obtained by Wöhler (1862) by heating carbon with an alloy of calcium and zinc. It is manufactured on a large scale by Moissan's process (1894). A mixture of 2 parts of coke and 3 parts of quicklime is heated to over 2000° in an electric furnace: $CaO + 3C = CaC_2 + CO$.

The furnace (Fig. 183) is a rectangular tank of fireclay divided into compartments lined with gas-carbon and having a graphite block in the base forming one electrode. The other electrode consists of vertical blocks of carbon suspended from chains and gradually lowered into the furnace as they are consumed. Arcs are struck between the base-plate and these electrodes, and the fused carbide is tapped, cooled, and broken into pieces in a jaw-crusher. The commercial carbide is greyish-black. According to Moissan (1903) the pure carbide is formed in colourless transparent crystals by heating calcium

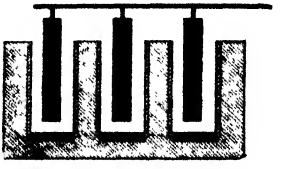


FIG. 183.—Calcium carbide furnace.

hydride in acetylene and the product in vacuum, but this is doubtful (Botolfsen, *Ann. Chim.*, 1922, **18**, 5). Calcium carbide is decomposed by water to give acetylene :

$$CaC_2 + 2H_2O = Ca(OH)_2 + C_2H_2 ;$$

1 kg. of commercial carbide usually gives about 300 litres of gas.

Calcium carbide is an energetic reducing agent. A powdered mixture with ferric oxide and ferric chloride burns violently when kindled with a taper, and fused metallic iron is produced.

Calcium carbonate $CaCO_3$ occurs in two crystalline forms : as hexagonal *calcite*, s.g. 2·71, and more rarely as rhombic *aragonite*, s.g. 2·93. Calcite occurs as limestone, calc-spar (Iceland spar is a pure transparent variety) and chalk ; marble consists of small interlocking calcite crystals (see Copisarow, *J.C.S.*, 1923, **123**, 785). Calcite is found in egg-shells and (with calcium phosphate) in bones. Aragonite occurs in mollusc shells and coral ; the mineral form usually contains strontium and lead carbonates. On passing carbon dioxide into cold lime water the flocculent amorphous precipitate soon crystallises as calcite ; from hot lime water aragonite separates. Calcite is the stable form at ordinary temperature and pressure ; it passes into aragonite above 400°.

Bivalent metal carbonates crystallise in the calcite form if the ion radius is 0·78–1·06 A. and the aragonite form if it is 1·06–1·43 A. Since the $Ca^{\cdot\cdot}$ ion radius is 1·06 $CaCO_3$ can crystallise in both forms. A third form μ-$CaCO_3$, s.g. 2·54, is said to be precipitated from lime water at 60° (Johnston, etc., 1916). When boiled for a few minutes with cobalt nitrate solution aragonite is coloured lilac but calcite is unchanged (Meigen, *J.C.S.*, 1901, **80**, ii, 692 ; 1905, **88**, ii, 454) ; an artificial hexagonal form of $CaCO_3$ called *vaterite* is also coloured.

An unstable hexahydrate $CaCO_3,6H_2O$ (said to occur in pearls and mother-of-pearl), a pentahydrate and perhaps a monohydrate are precipitated by carbon dioxide from lime water containing sugar (Hume, *J.C.S.*, 1925, **127**, 1036).

The solubilities in g./lit. are :

	8°	25°	100°
Calcite - - -	0·013	0·0143	0·01779
Aragonite - -	0·015	0·01528	0·01902

At 25° the solubility product is $[Ca^{\cdot\cdot}]\,[CO_3^{\cdot\cdot}] = 7{\cdot}2 \times 10^{-9}$ (Seyler and Lloyd, *J.C.S.*, 1917, **111**, 994).

In presence of carbon dioxide about 100 times as much calcium carbonate dissolves (0·94–1·08 g./lit. at 16° and 1 atm. ; Johnston and Williamson, *J.A.C.S.*, 1916, **38**, 975), a **bicarbonate** $Ca(HCO_3)_2$ being formed (Haehnel, 1924). A supersaturated solution is formed by passing carbon dioxide rapidly through saturated lime water (Cavazzi, 1916).

Flocculent precipitates of Ca, Sr and Ba bicarbonates, decomposing at room temperature, are said to be formed from $KHCO_3$ and strongly-cooled solutions of the chlorides (Keiser, etc., *J.A.C.S.*, 1908, **30**, 1711).

Calcium silicates shown in phase diagrams are two forms (α and β) of the **metasilicate** $CaSiO_3$ (CaO,SiO_2), an **orthodisilicate** $Ca_3Si_2O_7$ ($3CaO,2SiO_2$), a **basic metasilicate** $CaSiO_3,2CaO$, **tricalcium silicate** $3CaO,SiO_2$, and three (perhaps

four) forms of **orthosilicate** Ca_2SiO_4 ($2CaO,SiO_2$). There are also various hydrated forms.

Limestone containing more than 5 p.c. of clay on burning forms a lime which gives a *hydraulic mortar* which hardens under water. Vitruvius says the Romans used it for harbour works. In 1796 James Parker prepared *Roman cement* by heating clay and limestone below the sintering point. *Portland cement* (so called because after setting it resembles Portland stone) is made by heating a mixture of limestone and clay, either mixed with coal as in lime-burning, or by feeding the wet mixture into the top of a revolving inclined tubular furnace, into the lower part of which a blast of air charged with coal-dust, which forms an intense flame, is injected (Fig. 184). The materials sinter and the *cement clinker* formed is ground to powder.

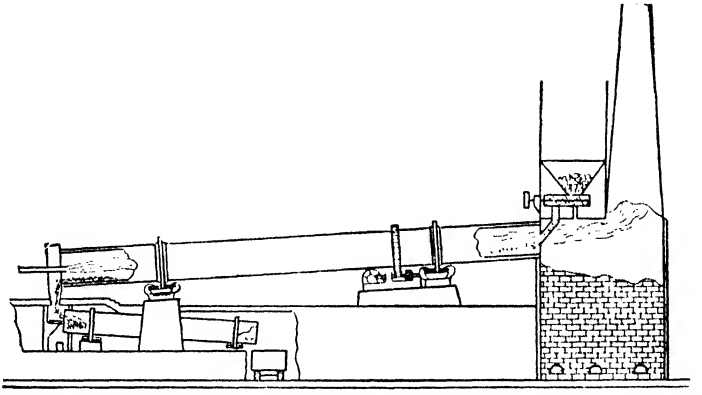


FIG. 184.—Cement furnace. The upper large tube is the furnace proper, the lower smaller tube, which also revolves, is a cooler.

The constitution and mode of setting of cement are complicated and have been variously explained (Bogue and Lerch, *Ind. Eng. Chem.*, 1934, **26**, 837). Cement clinker contains *tricalcium silicate* $3CaO,SiO_2$, *calcium orthosilicate* $2CaO,SiO_2$, *tricalcium aluminate* $3CaO,Al_2O_3$, and a *complex calcium aluminate* formerly thought to be $5CaO,3Al_2O_3$ but really $12CaO,7Al_2O_3$ (Büssem and Eitel, 1936; Thorvaldson and Schneider, *Canad. J. Res.*, 1941, **19**, 109). Some free lime and calcium aluminoferrite $4CaO,Al_2O_3,Fe_2O_3$ are also present.

When mixed with water, cement rapidly hydrates and sets to a gel of $3CaO,Al_2O_3,6H_2O$ and adsorbed water. The gel then slowly crystallises. The rapid increase in strength and hardness is mainly due to the partial hydrolysis of the tricalcium silicate to felted needles of calcium hydroxide in a gel of hydrated silicate. Addition of 2·5 p.c. of gypsum to the cement clinker before grinding retards the setting.

Glass.—Common *soda glass* contains calcium and sodium silicates and has the *approximate* composition $Na_2O,CaO,5SiO_2$ (Hodkin and Cousen, *Text-Book of Glass Technology*, 1925; on the sub-crystalline structure of glass see Warren, *Chem. Rev.*, 1940, **26**, 237). It is made by fusing sand, soda-ash (Na_2CO_3) and limestone, whiting or lime in fireclay pots or tanks at about 1375° C. or

higher. A mixture of saltcake (Na_2SO_4) and charcoal may replace soda-ash but is now less used :

$$2Na_2SO_4 + C + 2SiO_2 = 2Na_2SiO_3 + CO_2 + 2SO_2.$$

Ordinary glass contains a little aluminium oxide derived from the clay pots. The sand for the best glass must be white and free from iron compounds ; crushed quartz and broken flints are also used.

The green colour due to ferrous silicate may be neutralised by adding manganese dioxide or *pyrolusite* (Greek *pyr* fire, and *luo* I wash) ; this oxidises ferrous to ferric silicate, the yellow colour of which is masked by the purple colour due to manganese. Selenium and cobalt oxide are now used to decolorise bottle glass, and nickel oxide with flint glass.

Bohemian or *potash-glass* contains potassium instead of sodium, has a higher melting point and greater resistance to reagents, and is better adapted for chemical apparatus. *Flint-glass* is potash-glass with lime replaced by lead oxide (PbO). It has a high refractive index and is used for optical purposes but is very soft. *Jena resistance glass* has a low alkali and a higher alumina content (which confers toughness) than ordinary glass, contains barium and zinc oxides, and boron trioxide in place of some silica. *Pyrex glass*, resistant to heat and shock, is very rich in silica, poor in alkali and alumina, and contains boron trioxide. Toughened glass is obtained by cooling in oil.

Optical glasses contain boron trioxide and phosphorus pentoxide in place of silica, barium oxide in place of lime, and sometimes zinc oxide. Two main divisions are recognised : *crown glass* containing as basic oxide mainly potash or barium oxide, and *flint glass* containing lead oxide. *Crookes's glass* for spectacles contains rare-earth compounds (praseodymium and neodymium) : it allows visible light to pass but absorbs the ultra-violet. A very dark-red glass containing nickel absorbs nearly all visible light but allows some ultra-violet to pass. *Vita-glass*, which transmits some ultra-violet, is nearly free from iron and is made from very pure materials. Ordinary glass absorbs infra-red rays (radiant heat), hence its use for fire-screens.

Coloured glasses are made by adding various substances to the fused glass ; in the case of gold the colour develops only after reheating :

Red : gold, selenium, cuprous oxide.
Green : chromic oxide, cupric oxide with chromic or ferric oxides and a reducing agent.
Yellow : carbon and sulphates in the melt ; cadmium sulphide ; sometimes uranium or selenium.
Violet : manganese dioxide.
Blue : cupric oxide, cobalt oxide.
Opaque milky : fluorspar with felspar ; cryolite ; sometimes tin oxide or calcium phosphate.
Fluorescent greenish-yellow : uranium oxide.
Black : large quantities of ferric oxide and cupric oxide ; cobalt, nickel and manganese oxides.

Calcium nitride Ca_3N_2 is a brownish-yellow solid, m.p. 1195°, formed by passing nitrogen over calcium at 450° or rapidly with fused calcium. It is decomposed by steam : $Ca_3N_2 + 6H_2O = 2NH_3 + 3Ca(OH)_2$. On heating, $Ca(NH_3)_6$ (p. 369) forms the **amide** : $Ca(NH_3)_6 = Ca(NH_2)_2 + 4NH_3 + H_2$, and on heating

this in high vacuum a reddish-yellow **pernitride** Ca_3N_4 is formed, decomposed by water (Hartmann, Frölich and Ebert, 1934) :

$$Ca_3N_4 + 6H_2O = 3Ca(OH)_2 + 2NH_3 + N_2.$$

At 400° at ordinary pressure $Ca(NH_2)_2$ gives the **imide** CaNH.

Calcium nitrate $Ca(NO_3)_2$ is present in the soil and is used as a fertiliser. It is manufactured by neutralising dilute nitric acid with limestone and evaporating, also by passing oxides of nitrogen into milk of lime or a suspension of calcium carbonate in water until the nitrite in the mixture is decomposed (p. 569). It forms very deliquescent monoclinic crystals $Ca(NO_3)_2,4H_2O$ (two forms, m.ps. 42·7° and 39·7°) soluble in alcohol. According to T. W. Richards the best method of obtaining a pure calcium salt is repeated crystallisation of the nitrate from water or alcohol. The anhydrous salt, m.p. 561°, dissolves in amyl alcohol. There are also tri- and di-hydrates and a basic nitrate $Ca(NO_3)_2,CaO$ and hydrates (Bassett and Taylor, *J.C.S.*, 1914, **105**, 1926). Calcium nitrate decomposes on heating, leaving calcium oxide.

Calcium phosphide Ca_3P_2 is formed in red crystals by passing phosphorus vapour over heated calcium or heating calcium phosphate with carbon in the electric furnace (Moissan, 1899). It gives pure phosphine PH_3 with water. The *crude* phosphide, containing Ca_2P_2 and calcium pyrophosphate, is made by passing phosphorus vapour over heated quicklime : $14P + 14CaO = 5Ca_2P_2 + 2Ca_2P_2O_7$; it gives with water spontaneously inflammable phosphine containing P_2H_4 (p. 601).

Calcium phosphate $Ca_3(PO_4)_2$ occurs in bones and in the mineral *phosphorite*. It is formed as a white amorphous flocculent precipitate on adding ammonium phosphate and a large excess of ammonia to calcium chloride solution : $3Ca^{\cdot\cdot} + 2HPO_4'' + 2OH' = Ca_3(PO_4)_2 + 2H_2O$, but the precipitate may be the basic phosphate $3Ca_3(PO_4)_2,Ca(OH)_2$ or $[Ca\{Ca_3(PO_4)_2\}_3](OH)_2$, *hydroxyapatite* (Eisenberger, *Chem. Reviews*, 1940, **26**, 257). Anhydrous $Ca_3(PO_4)_2$, m.p. 1670°, is shown by the high-temperature phase diagram and X-ray spectrum (Bredig, Franck and Füldner, *Z. Elektrochem.*, 1932, **38**, 158 ; Trömel and Möller, *Z. anorg. Chem.*, 1932, **206**, 227). Calcium phosphate is nearly insoluble in water, but dissolves in water containing many salts or carbon dioxide, which dissolve the calcium phosphate in the soil and render it capable of absorption by the roots of plants.

Ordinary sodium phosphate, or better a mixture of $NH_4H_2PO_4$ and $(NH_4)_2HPO_4$ (Bassett, *Z. anorg. Chem.*, 1907, **53**, 34, 49 ; 1908, **59**, 1 ; *J.C.S.*, 1917, **111**, 620), precipitates from a calcium salt solution **calcium hydrogen phosphate** $CaHPO_4$ either anhydrous or with $4H_2O$ according to conditions : $Na_2HPO_4 + CaCl_2 = CaHPO_4 + 2NaCl$. This and the normal phosphate dissolve in aqueous phosphoric acid and on spontaneous evaporation the solution deposits crystals of **calcium dihydrogen phosphate** $Ca(H_2PO_4)_2,H_2O$:

$$Ca_3(PO_4)_2 + 4H_3PO_4 \rightleftharpoons 3Ca(H_2PO_4)_2$$
$$CaHPO_4 + H_3PO_4 \rightleftharpoons Ca(H_2PO_4)_2.$$

This is decomposed by water by the reverse of these reactions. It loses water at 100°–105°. Pure calcium dihydrogen phosphate (also called **monocalcium**

phosphate) is made commercially by dissolving slaked lime or pure limestone in phosphoric acid, crystallising and drying, and is used in American baking powder.

A mixture of the acid phosphate $Ca(H_2PO_4)_2$, anhydrous calcium sulphate $CaSO_4$ and phosphoric acid is the fertiliser called *superphosphate of lime* (Hill and Hendricks, *Ind. Eng. Chem.*, 1936, **28**, 440). It is made by macerating ground mineral calcium phosphate (*phosphorite*) with two-thirds of its weight of 70 p.c. sulphuric acid :

$$5Ca_3(PO_4)_2 + 11H_2SO_4 = 4Ca(H_2PO_4)_2 + 2H_3PO_4 + 11CaSO_4.$$

The reaction is carried out in a horizontal cast-iron cylinder with revolving blades. The mixture issues nearly fluid into pits or *dens*, which are half-filled and then closed. Reaction occurs with rise of temperature and gases (CO_2, SiF_4, HF, and HCl) escape through a vent to absorption towers. After a day or two the superphosphate is removed, powdered, and carefully dried by hot air in long brickwork chambers.

Apatite (Greek *apatao*, I deceive, old mineralogists having confused it with many other species) is properly the name of the mineral $3Ca_3(PO_4)_2,CaF_2$, but is now applied (with the names *fluorapatite*, *chlorapatite*, etc.) to a group of compounds $3Ca_3(PO_4)_2,CaX$ where X may be F_2, Cl_2, $(OH)_2$, CO_3, SO_4, etc. (Ditte, *Ann. Chim.*, 1886, **8**, 502), formulated by Werner (*Ber.*, 1907, **40**, 4441) as $[Ca\{Ca_3(PO_4)_2\}_3]X$. Related compounds (see p. 236) are *mimetite* (formerly called *mimetisite*) $[Pb\{Pb_3(AsO_4)_2\}_3]F_2$, *pyromorphite* $[Pb\{Pb_3(PO_4)_2\}_3]Cl_2$, *vanadinite* $[Pb\{Pb_3(VO_4)_2\}_3]Cl_2$, and *wagnerit* $[Mg\{Mg_3(PO_4)_2\}_2]F_2$ (only two coordination positions occupied). **Basic calcium phosphate** $Ca_4P_2O_9$ or $Ca_3(PO_4)_2,CaO$ is a constituent of *basic slag* (p. 842) and may be formulated as $[Ca\{Ca_3(PO_4)_2\}]O$ (only one coordination position occupied) ; it appears on the freezing-point diagram as a definite compound.

Calcium sulphide CaS (present in the *alkali waste* of the Leblanc process, p. 306) is prepared (i) by heating gypsum with charcoal at 900° : $CaSO_4 + 4C = CaS + 4CO$, or in hydrogen at 600°–800° : $CaSO_4 + 4H_2 = CaS + 4H_2O$ (above 900° the sulphide and sulphate react : $CaS + 3CaSO_4 = 4CaO + 4SO_2$), (ii) in the pure state by passing hydrogen sulphide over gently heated slaked lime : $Ca(OH)_2 + H_2S = CaS + 2H_2O$. Calcium sulphide is a white apparently amorphous solid, but the X-ray spectrum indicates a rock-salt lattice. The sulphide containing traces of heavy metals is phosphorescent (p. 390). Calcium sulphide is sparingly soluble (0·2 g. per lit. at 20°) and is hydrolysed :

$$2CaS + 2H_2O = Ca(OH)_2 + Ca(HS)_2.$$

It dissolves when hydrogen sulphide is passed into the suspension, forming **calcium hydrosulphide** $Ca(HS)_2$. This crystallises as $Ca(HS)_2,6H_2O$ when hydrogen sulphide is passed (in absence of air) into a thick paste of calcium hydroxide, calcium oxide being added as this dissolves : it is soluble in water and alcohol. **Calcium hydroxy-hydrosulphide** $Ca(OH)(HS),3H_2O$ is formed by decomposing the hydrosulphide with water :

$$Ca(HS)_2 + H_2O = Ca(OH)(HS) + H_2S :$$

it is insoluble in alcohol (Divers and Shimidzu, *J.C.S.*, 1884, **45**, 270).

Calcium polysulphides CaS_2 to CaS_5 or possibly CaS_7 are contained in the reddish-yellow solution (*thion hudor*, p. 693) made by boiling sulphur with milk of lime (Auld, *J.C.S.*, 1915, **107**, 480) :

$$12S + 3Ca(OH)_2 = 2CaS_5 + CaS_2O_3 + 3H_2O$$
$$4S + Ca(OH)_2 + CaS_2O_3 = CaS_5 + CaSO_4 + H_2O.$$

Crystals of *Herschel's salt*, $CaS_4,3Ca(OH)_2,9H_2O$ (Schöne, 1862), or $CaS_3,2Ca(OH)_2$, 8 or $9H_2O$ (Geuther, 1884), or $CaS_2,Ca(OH)_2,6H_2O$ (Auld, 1915), separate from the concentrated solution.

Buchner's salt, formed in various ways, is $CaS_4,4Ca(OH)_2,14H_2O$ (Schöne) or $CaS_3,3Ca(OH)_2$, 11 or $12H_2O$ (Geuther).

Calcium sulphate occurs as rhombic *anhydrite* $CaSO_4$, s.g. 2·94, and more commonly as monoclinic *gypsum* $CaSO_4,2H_2O$, s.g. 2·32, either in transparent crystals of *selenite* (often twinned) or crystalline masses either fibrous (*satin spar*) or opaque (*alabaster*) (see Copisarow, *J.C.S.*, 1923, **123**, 796).

Anhydrous calcium sulphate exists in two forms : (*a*) natural anhydrite and that formed by dehydrating gypsum at a red heat, both practically insoluble ; (*b*) a soluble form, " setting " with water, produced by dehydrating gypsum at 60°–90° in vacuum over P_2O_5.

The solubilities of gypsum in g. $CaSO_4$ per 100 g. H_2O are :

0°	10°	30°	40°	50°	60°
0·176	0·193	0·209	0·210	0·204	0·200

Gypsum can easily be reduced to an extremely fine powder and the solubility increases with the fineness of the grains. This is due to surface-tension forces, which are more pronounced with small particles. The solubility increases with temperature to 40°, and diminishes at higher temperatures. (Hulett, *J.A.C.S.*, 1905, **27**, 49 ; W. J. Jones and Partington, *Phil. Mag.*, 1915, **29**, 35 ; M. Jones and Partington, *J.C.S.*, 1915, **107**, 1019 ; Namba, *J.S.C.I.*, 1920, **40**, 279T.)

Gypsum at 120°–130° loses water and forms *plaster of Paris*, the hemihydrate $CaSO_4,\frac{1}{2}H_2O$, which when mixed with water evolves heat and quickly solidifies to gypsum, expanding slightly ; it is used for casts. Plaster of Paris at 140° begins to lose water, all of which is rapidly expelled at 200°. The residue of anhydrous $CaSO_4$, s.g. 2·57, rapidly takes up water, but if more strongly heated it hydrates only very slowly (like natural anhydrite) and is said to be " dead-burnt " : its s.g. is then 2·96. By heating over 400° slight decomposition into CaO and SO_3 occurs and *estrich plaster* is formed : this sets slowly to a smooth hard surface and is used for floors, walls, etc.

Calcium sulphate hemihydrate $CaSO_4,\frac{1}{2}H_2O$ can be obtained in rhombic prisms, s.g. 2·75, by heating for some time on a water bath 20 g. of gypsum and 50 c.c. of conc. HNO_3 (van't Hoff and Armstrong, *Z. phys. Chem.*, 1903, **45**, 257) : it is a definite compound with a characteristic X-ray spectrum (Weiser and Milligan, *J.A.C.S.*, 1936, **58**, 1261 ; 1937, **59**, 1456 ; Dunn, *J.S.C.I.*, 1938, **57**, 144 ; cf. Davis, *ibid.*, 1907, **26**, 727), and there is a corresponding selenate (Meyer and Aulich, 1928).

Calcium sulphate begins to dissociate at 960° ; when mixed with silica it reacts at 870° and rapidly at 1280° : $CaSO_4 + SiO_2 = CaSiO_3 + SO_3$. Hydrogen chloride decomposes it at a red heat, forming $CaCl_2$.

Precipitated gypsum formed by adding sulphuric acid to a solution of calcium chloride is used as *pearl-hardening* for " filling " glazed paper. Ordinary blackboard " chalk " is made from gypsum.

The double salts $CaSO_4,K_2SO_4,H_2O$ (*syngenite*), $CaSO_4,Na_2SO_4$ (*glauberite*), and $CaSO_4,2Na_2SO_4$, are known. Calcium sulphate dissolves in a concentrated solution of ammonium sulphate forming $CaSO_4,(NH_4)_2SO_4,H_2O$. Strontium and barium sulphates are insoluble.

Calcium sulphite $CaSO_3$ is formed as a white precipitate (solubility 0·24 g./lit. at 25°) by passing sulphur dioxide into a fairly large volume of lime water, or by mixing solutions of sodium sulphite and calcium chloride. It dissolves in sulphurous acid forming **calcium hydrogen sulphite** $Ca(HSO_3)_2$, prepared by passing sulphur dioxide in excess into milk of lime and used in sterilising beer casks and in the manufacture of wood-pulp. On standing exposed to air the solution deposits crystals of $CaSO_3,2H_2O$.

Calcium thiosulphate is formed on passing air through a suspension of the sulphide. On adding 350 g. of $CaCl_2,2H_2O$ in fine crystals to 510 g. of sodium thiosulphate in 465 g. of water, allowing to stand overnight, filtering and cooling to −10°, crystals of $CaS_2O_3,6H_2O$ separate (Bichowsky, *J.A.C.S.*, 1923, **45**, 2225).

Strontium and Barium

The commomest barium mineral is the sulphate $BaSO_4$, *barytes* or *heavy spar*, s.g. 4·5 (Greek *barus*, heavy), which occurs in rhombic crystals and often with galena. In 1602 Vincenzo Cascíorolo, a shoemaker of Bologna, found that it gave a phosphorescent solid (BaS) when heated with charcoal : $BaSO_4 + 4C = BaS + 4CO$. Scheele in 1774 discovered a new " earth " (BaO) in native manganese dioxide (which contains barium as an impurity, p. 820) and Gahn in 1775 found that it is contained in heavy spar. It was called *barote* by Guyton de Morveau and *barytes* by Kirwan. Barium carbonate $BaCO_3$ occurs as *witherite*, s.g. 4·28, rhombic, isomorphous with aragonite and found in lead mines. *Alstonite* is a rhombic and *barytocalcite* a monoclinic form of $BaCO_3,CaCO_3$.

A peculiar " earth " was found in a mineral from a lead mine at Strontian in Argyllshire by Crawford in 1790, and was called *strontites* by Hope and *strontia* by Klaproth (Partington, *Annals of Science*, 1942, **5**, 157). The mineral is *strontianite* or strontium carbonate $SrCO_3$, isomorphous with aragonite ; strontium sulphate $SrSO_4$ occurs as rhombic *celestine*, s.g. 3·9, so called from the pale blue colour of some specimens. Metallic strontium and barium were isolated electrolytically by Davy in 1808.

Barium compounds are poisonous but they occur in plants (especially the leaves of some trees) and in the eyes of various animals. Strontium compounds are not poisonous. Strontium and barium salts are prepared from the native carbonates or sulphates.

The carbonate is dissolved in hydrochloric acid, iron oxidised by chlorine and precipitated as ferric hydroxide by boiling with a little strontium or barium carbonate (precipitated from some of the solution by sodium carbonate), and the filtrate evaporated, when strontium chloride $SrCl_2,6H_2O$ or barium chloride $BaCl_2,2H_2O$ crystallises.

The sulphates are sparingly soluble ($SrSO_4$) or insoluble ($BaSO_4$) in acids. They may be fused with excess of sodium carbonate and the carbonate $SrCO_3$ or $BaCO_3$ washed with hot water and dissolved in dilute hydrochloric or nitric acid. The sulphates may also be heated strongly with carbon and the sulphides formed dissolved in acids.

Metallic strontium and barium are best prepared (Guntz, 1907; Danner, *J.A.C.S.*, 1924, **46**, 2382) by heating the oxide (SrO, or BaO containing 10 p.c. of BaO_2) with aluminium powder in an iron tube at 1400° in vacuum and condensing the vapour on a water-cooled polished steel tube. Strontium is freely volatile at 950° and barium at a lower temperature. Barium is also obtained by heating the oxide with silicon in an evacuated steel tube at 1200° (Matignon, 1913).

Strontium and barium are silver-white and soft. Barium when finely divided inflames in air and strontium is nearly as reactive. They combine directly with hydrogen and nitrogen.

Strontium and barium **hydrides** SrH_2 and BaH_2 are formed when the metals or their amalgams are heated in hydrogen (barium even at room temperature). They are white solids decomposing on heating in vacuum and the pure metals may be condensed on a polished steel water-cooled tube. The **nitrides** Sr_3N_2 and Ba_3N_2 (yellow) are decomposed by water with formation of hydroxides and ammonia.

Halides

SrF_2, cubic, m.p. 1400°.
$SrCl_2$, cubic, m.p. 873°, crystallising with 6 (common), 2 and $1H_2O$.
$SrBr_2$, m.p. 643°, crystallising with 7, 6 (common) and $1H_2O$.
SrI_2, m.p. 507°, crystallising with 6 (common), 2 and $1H_2O$.
BaF_2, cubic, m.p. 1280°.
$BaCl_2$, monoclinic, cubic above 924·5°, m.p. 959°, crystallising with 2 (common) and $1H_2O$.
$BaBr_2$, m.p. 847°, crystallising with $2H_2O$.
BaI_2, m.p. 740° with decomp., crystallising with 6 and 2 (common, rhombic) H_2O.

Anhydrous strontium chloride is sparingly soluble in alcohol, which however separates it from the insoluble barium chloride, which is moderately soluble in methyl alcohol. The bromides and iodides are readily soluble in alcohol. Crystalline $SrCl_2,6H_2O$ (hexagonal) and $BaCl_2,2H_2O$ (monoclinic) are stable in air.

The solubilities of the hydrates in g. anhyd. salt in 100 g. H_2O are:

	0°	10°	20°	30°	40°	60°	80°	100°
$SrCl_2$	44·3	48·4	53·8	60·0	66·6	83·2	92·3	102·0
$BaCl_2$	31·6	33·3	35·7	38·1	40·8	46·4	52·5	58·7

The solubility in hydrochloric acid is much smaller, and concentrated hydrochloric precipitates barium chloride from solution (which must be remembered in testing for sulphates).

Oxides and Hydroxides

Strontium and barium oxides SrO and BaO are obtained by heating the nitrates (strongly with barium, otherwise BaO_2 is formed) and pure BaO by heating the iodate. Strontium oxide is formed by heating the hydroxide or strongly heating the carbonate, but these reactions are unsatisfactory with barium compounds, which are more stable. The carbonates are more easily decomposed when heated with carbon: $BaCO_3 + C = BaO + 2CO$, and barium carbonate when heated in steam gives the hydroxide: $BaCO_3 + H_2O = Ba(OH)_2 + CO_2$.

Strontium and barium oxides are white amorphous solids like quicklime but more fusible; they can form cubic crystals. They absorb moisture and carbon dioxide from the air and combine with water with evolution of heat to form crystalline basic hydroxides.

Strontium hydroxide $Sr(OH)_2,8H_2O$, tetragonal, is fairly soluble in hot water; it dehydrates by efflorescence to $Sr(OH)_2,H_2O$, which at 100° forms $Sr(OH)_2$ and this dehydrates to the oxide SrO at 710°.

Barium hydroxide $Ba(OH)_2,8H_2O$, monoclinic, is readily soluble in hot water; it effloresces in dry air to $Ba(OH)_2,H_2O$ and this dehydrates to $Ba(OH)_2$ at 100° in a current of dry air. Crystals of $Ba(OH)_2,3H_2O$ separate from a boiling solution. Barium hydroxide $Ba(OH)_2$ melts below 650° but does not lose water to form BaO unless very strongly heated or heated in a current of hydrogen above 850°. The solution of barium hydroxide (*baryta water*) gives a white precipitate of $BaCO_3$ with carbon dioxide.

Barium hydroxide is used in volumetric analysis, since any carbonate formed by exposure to air is precipitated and does not interfere with colour-changes of indicators.

Strontium hydroxide is used in sugar-refining as it forms a sparingly soluble saccharate $C_{12}H_{22}O_{11},2SrO$ with cane sugar, a suspension of which in water is decomposed into sugar and strontium carbonate by carbon dioxide. Magnesium, calcium and barium hydroxides form similar compounds.

Strontium and barium form **peroxides** SrO_2 and BaO_2 (tetragonal), and these form crystalline hydrates (tetragonal) with $8H_2O$.

Barium peroxide BaO_2 (Gay-Lussac and Thenard, 1811; Brodie, *Phil. Trans.*, 1863, **153**, 409) is formed by passing air or oxygen free from moisture and carbon dioxide over baryta heated to dull redness: $2BaO + O_2 \rightleftharpoons 2BaO_2$, and by heating baryta with potassium chlorate (Liebig and Wöhler, 1832). The dissociation pressures of BaO_2 are:

555°	650°	720°	790°	795° C.
25	65	210	670	760 mm.

Strontium peroxide SrO_2 is formed from the monoxide and oxygen at 400° under 125 kg./sq. cm. pressure. (Calcium peroxide has not been obtained directly.) The hydrates $BaO_2,8H_2O$ and $SrO_2,8H_2O$ are obtained as crystalline precipitates by adding hydrogen peroxide to cold saturated solutions of barium and strontium hydroxides. On heating they lose water and form BaO_2 and SrO_2.

By precipitating a concentrated solution of the hydroxide above 50°, anhydrous SrO_2 is formed; below 40° the compounds BaO_2,H_2O_2 or BaO_3,H_2O (yellow) and $BaO_2,2H_2O_2$ or $BaO_4,2H_2O$ are formed with excess of hydrogen peroxide and baryta water.

Strontium and Barium Salts

Strontium and **barium carbonates** $SrCO_3$ and $BaCO_3$ are formed as white precipitates by passing carbon dioxide into solutions of the hydroxides, redissolving with excess of carbon dioxides and forming **bicarbonates** $Sr(HCO_3)_2$ and $Ba(HCO_3)_2$. The carbonates are more stable than calcium carbonate; barium carbonate decomposes only at very high temperatures, and can be heated with a blowpipe without any appreciable change (cf. Jones and Becker, *J.C.S.*, 1927, 2669); it attacks platinum at a red heat.

The dissociation pressures of strontium carbonate are:

$t°$ C. -	650	850	950	1050	1258	1263
p mm. -	18	50	99	175	760	785

and of barium carbonate:

$t°$ C. -	915	1020	1120	1220	1300	*c.* 1352
p mm. -	0·4	4·3	24·4	114	381	760

The solubility of strontium carbonate is 0·010 g./lit. at 15°, the solution being somewhat hydrolysed. Various figures are given for barium carbonate, which undergoes some hydrolysis: Fresenius gave 0·071 g./lit. at 18°. A suspension of barium carbonate precipitates ferric, chromic and aluminium hydroxides from solutions of the salts but does not precipitate zinc or manganese salts.

Strontium and **barium nitrates** $Sr(NO_3)_2$ and $Ba(NO_3)_2$ separate in cubic crystals from solutions of the carbonates in dilute nitric acid on evaporation (strontium nitrate crystallises with $4H_2O$ below 32°). They are used in pyrotechny mixed with charcoal and sulphur to make red and green fires, respectively. Strontium nitrate at the m.p. 645° gives mostly the nitrite $Sr(NO_2)_2$ but barium nitrate, m.p. 593°, on heating gives mostly oxide and peroxide and only a little nitrite.

Strontium or barium salts are freed from calcium by precipitating solutions of the nitrates with alcohol, in which calcium nitrate is soluble. Barium nitrate is less soluble in water than strontium nitrate; it is precipitated from saturated barium chloride solution by nitric acid. Strontium nitrate is less soluble than calcium nitrate. A pure barium compound is best obtained by repeated crystallisation of the nitrate and precipitating barium carbonate with ammonium carbonate; strontium nitrate is freed from barium by adding calcium sulphate solution, filtering, and crystallising.

Strontium and **barium phosphates** (Tartar and Lorah, *J.A.C.S.*, 1929, **51**, 1091) are similar to the calcium salts.

Strontium and **barium sulphides** SrS and BaS are formed by strongly heating the sulphates with carbon or the carbonates in a mixture of carbon dioxide and carbon disulphide vapour. Strontium sulphide is used for phosphorescent

material (p. 390). Pure barium sulphide is formed by heating $Ba(OH)_2,H_2O$ in hydrogen sulphide at 200° (Veley, *J.C.S.*, 1886, **49**, 369). The pure sulphides are white soluble powders hydrolysed by water :

$$2BaS + 2H_2O \rightleftharpoons Ba(HS)_2 + Ba(OH)_2.$$

The **hydrosulphides** are formed by passing hydrogen sulphide into solutions of the sulphides, and crystallise as $Sr(HS)_2,4H_2O$ and $Ba(HS)_2,4H_2O$. Various polysulphides are known (Robinson and Scott, *J.C.S.*, 1931, 693).

Strontium sulphate $SrSO_4$, m.p. 1605°, is less soluble (0·1 g./lit. at 15°) than calcium sulphate but much more soluble than barium sulphate. Strontium sulphate is less soluble in dilute sulphuric acid than in water, but more soluble in other acids and salt solutions, including strontium salts (0·198 g./lit. in 10 p.c. strontium nitrate). It is practically insoluble in alcohol.

Barium sulphate $BaSO_4$ (rhombic, monoclinic above 1149°) is formed from sulphuric acid or a sulphate and a barium salt solution as a fine white precipitate almost insoluble in water (0·0024 g./lit. at 15°) and acids, except hot concentrated sulphuric and hydrochloric acids. The acid sulphate $Ba(HSO_4)_2$ can be crystallised from the solution in sulphuric acid. Barium sulphate is used as a pigment (*blanc fixe* or *permanent white*), although it has a poor covering power, and as a glaze for paper.

Barium sulphate carries down various soluble salts, especially potassium and other sulphates, salts of tervalent metals (Fe, Cr), nitrates and chlorates, which cannot be removed by washing. It adsorbs barium chloride and is slightly soluble in dilute hydrochloric acid and in many salt solutions. Barium sulphate is only slightly decomposed at 1300° ; it melts at 1580° and decomposes at 1600°. Barium and strontium sulphates are converted into carbonates by boiling with alkali carbonate solution, and the reaction is reversible. Barium sulphate is almost quantitatively converted to carbonate on fusion with 8–9 mols. of K_2CO_3, but barium carbonate is only very incompletely converted into sulphate on fusion with K_2SO_4.

CHAPTER XV

ZINC, CADMIUM AND MERCURY

THE metals of sub-group *b* (odd series) of Group II, zinc, cadmium and mercury, differ in many ways from the alkaline earth metals of sub-group *a* (even series), and in themselves form a group with close resemblances among its members but a decided gradation of properties in accordance with the increase of electropositive character with atomic weight (p. 179).

Zinc

Plato (400 B.C.) refers to *orichalcum* as a metal known long before his time. This was probably *brass*, obtained by heating copper with an ore *cadmia* and charcoal. Brass of 1500 B.C. containing 23 p.c. of zinc and 10 p.c. of tin was found at Gezer in Palestine. Cadmia, called *tutia* by the alchemists, was probably zinc carbonate or oxide. The name is said to occur as *tusku* on Assyrian tablets of 650 B.C. Deposits of *calamine*, or native zinc carbonate, occur in the old silver mines of Laurion in Greece, and Strabo (about 7 B.C.) describes the preparation of the metal, which he calls "mock-silver," by heating the oxide with coal. A statuette from Thrace of about his time consists of zinc with 11·5 p.c. of lead and a little iron.

In the seventeenth century Boyle calls zinc *spelter* and Libavius reports it as a kind of tin, called *calaëm* in the East Indies. The existence of zinc in zinc blende was recognised by Homberg in 1695, and Kunckel (d. 1703) says "calamine allows its mercurial [metallic] part to pass into copper and form brass." Zinc extraction was early in India and China and zinc was made from calamine by Isaac Lawton in 1730, the first European zinc works being started by John Champion at Bristol in 1743. Zinc smelting began at Liége in Belgium in 1807 and later in Silesia.

Traces of native zinc occur in Melbourne, Australia. The chief ore is the sulphide ZnS, *blende* (*sphalerite* in the U.S.A.): it is usually coloured yellow or brown by iron and has a resinous lustre. It is found in many parts of Europe and America: Belgium and Silesia, and Oklahoma, are the main producers; it is also found in Canada, Rhodesia, Burma and New South Wales.

Zinc carbonate $ZnCO_3$ occurs as *calamine* (*smithsonite* in the U.S.A.); the anhydrous silicate Zn_2SiO_4 is *willemite*, the hydrated silicate Zn_2SiO_4,H_2O is *electric calamine* or *hemimorphite* (*calamine* in the U.S.A.). The oxide ZnO is *zincite* or *red zinc ore* and is rare, but the ferrite $Zn(FeO_2)_2$ forms the important *franklinite* deposit at Franklin Furnace, New Jersey, mostly worked for zinc oxide and the manganese it also contains. New South Wales blende contains galena and is first concentrated by flotation. Some pyrites (*e.g.* Westphalian) contain zinc, as do many copper, silver, and platinum ores.

Traces of zinc occur as an organic compound in animal cells and in snake venom (0·11–0·56 p.c.)

Zinc is a volatile metal and is obtained by a distillation process, the oxide being strongly heated with carbon: $ZnO + C = Zn + CO$. The *Belgian* and the *Silesian* processes differ according to the type of retort used.

The ore is roasted by external heating, the blende being raked in a series of muffles through which air circulates, or on a furnace hearth. Care must be taken to form only oxide: $2ZnS + 3O_2 = 2ZnO + 2SO_2$, as the sulphate is very stable and in the subsequent reduction would again form sulphide. The sulphur dioxide is used to make sulphuric acid. Some sulphate formed in roasting is decomposed at the high temperature used. The roasted ore is mixed with half its weight of powdered coal and distilled in rather small fireclay retorts which are strongly heated. Reduction begins below 800° and is rapid at 1033°; the working temperature may reach 1500°.

The *Belgian retorts* are fireclay tubes closed at one end and set sloping down towards the open end. A fireclay tube is luted into the open end with clay and serves to condense the zinc vapour. The *Silesian retorts* are fireclay muffles, and beyond the fireclay condenser is an iron "prolong" from which the carbon monoxide burns (Fig. 185). The newer *Belgo-Silesian furnaces* have three rows of

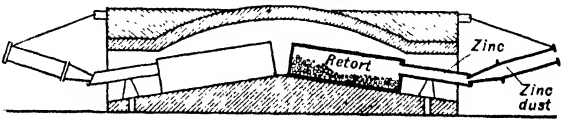


FIG. 185.—Zinc furnace.

muffles, one above the other, the lower row being supported along their lengths on the hearth and the two upper rows only at the ends. They are fired with gas. The temperature of the receivers must be 415°–550° if molten zinc is to be formed. Below 415° only zinc dust separates, above 550° nothing condenses. In all cases 10–25 p.c. of zinc is lost, about half in the ash and half as vapour.

The oxide is also smelted to a limited extent, *e.g.* in British Columbia, in electric furnaces of the arc or resistance type, but much zinc is then obtained mixed with oxide as *zinc dust*, which is also produced to a less extent in fuel-fired furnaces.

Commercial zinc or *spelter* contains about 97–98 p.c. of zinc, 1–3 p.c. of lead, up to 0·1 p.c. of iron, more rarely cadmium and some arsenic. Fusion with nitre removes arsenic and some iron. Pure zinc is prepared by electrolysis of an acid solution of zinc sulphate with a high current density (Pring and Tainton, *J.C.S.*, 1914, **105**, 710).

The deposition voltage of zinc is 0·785, higher than the *reversible* deposition voltage of hydrogen. But the overvoltage of hydrogen on zinc is large (1·23 volts in *N* acid), hence zinc deposits. The electrolyte must be very pure. Antimony and cobalt are very prejudicial: 1 part per million of antimony, germanium or arsenic affects the result. The effect of cobalt may be counteracted by adding glue. The voltage is 3·25–3·5, the current density is 20–30 amp. per

sq. ft., lead anodes and pure aluminium cathodes being used. The zinc is stripped from the cathodes; the deposit is bright with 2–3 p.c. of free acid and the bath is not allowed to run above 0·66 *N* acid. The best grade of electrolytic zinc should not contain more than 0·005 p.c. iron and 0·05 p.c. lead; the cadmium content depends on the purity of the solution but the metal is usually 99·9 p.c. zinc.

Even 99·9 p.c. electrolytic zinc is not good enough for the best grades of brass free from the defect of "season cracking," and "crown special" 99·99 p.c. zinc is made by fractional distillation by the National Smelting Company at Avonmouth, near Bristol. The chief impurities in zinc are iron (b.p. 2800°), lead (b.p. 1620°) and cadmium (b.p. 767°). The cadmium can be completely vaporised below the b.p. of zinc (920°).

The molten zinc is fed into a column heated above its boiling point when most of the zinc and all the cadmium distil and are condensed, the iron and lead collecting in the zinc leaving the base of the column. The distilled zinc is now fed to a second column, in which cadmium distils and the very pure zinc flows from the base of the column.

Zinc is produced directly from blende by roasting below 650° to oxide (and a little sulphate), leaching with dilute sulphuric acid and spent electrolyte, precipitating Fe, Al, As, Sb and SiO_2 by milk of lime, and Cu and Cd by zinc dust (excess is used to precipitate all the cadmium, which is recovered). The liquid is filtered and goes to the electrolytic cells, some spent acid electrolyte being added.

Zinc dust is formed in the furnaces or is made by atomising molten zinc with a blast of air, and consists of small spheres of zinc coated with oxide. The good kinds may contain over 90 p.c. of metal and the rest oxide. Zinc nitride may be present. Zinc oxide may be removed by washing with very dilute hydrochloric acid, water and alcohol, and drying. Zinc is granulated by melting and pouring into water. Zinc sheet or foil is made by softening the metal by heating at 100°–150° and rolling it.

Ordinary zinc dissolves easily in dilute acid but some varieties of very pure metal only slowly unless in contact with metallic copper or platinum, or if these metals are deposited on the zinc, forming a galvanic couple, by adding copper sulphate or platinic chloride solution to the acid. The zinc dissolves and hydrogen gas is deposited on the other metal (de la Rive, 1830). Amalgamated zinc is hardly attacked by acids (Sturgeon, 1830) and is made by rubbing the zinc with mercuric nitrate solution. Some kinds of commercial zinc are more resistant when amalgamated than is the pure metal (J. N. Friend, 1929).

Zinc crystallises in hexagonal prisms (only one form is known), s.g. 7·14, m.p. 419·4°, b.p. 920°: the vapour is monatomic. Zinc is fairly hard and brittle; it softens at 100°–150° but becomes very brittle at 205° and can then be powdered in a mortar. Zinc burns in air with a green flame when the turnings are heated in a flame or the metal vaporised in a crucible, the oxide settling in white woolly flocks called *pompholix*, philosophers' wool, *nix alba* (white snow), or *nihilum album*. The metal oxidises in moist air to a greyish-white crust of basic carbonate $ZnCO_3,3Zn(OH)_2$. It is attacked by ordinary soft water and especially by water containing peat acids and by sea water. It remains bright in distilled water free from air. The zinco-solvency of fresh water is reduced by standing over limestone (Davies, *J.S.C.I.*, 1899, **18**, 102;

Moody, *Proc. C.S.*, 1903, **19**, 273; Dunstan and Hill, *J.C.S.*, 1911 **99**, 1835). Red-hot zinc decomposes steam but the reaction is reversible and zinc oxide is reduced above 450° in a rapid stream of *dry* hydrogen:

$$Zn + H_2O \rightleftharpoons ZnO + H_2.$$

Zinc is more resistant to moist air than iron, which is *galvanised* or plated with zinc to prevent rusting.

The iron sheets or wire are cleaned and dipped in molten zinc, when an adherent coating is formed. Iron articles may be coated with zinc by spraying, or by heating in zinc dust (*sherardising*), and bright electroplating from cyanide baths is also used. The zinc oxidises before iron, since it has a higher solution pressure. Zinc is used for the negative electrodes of voltaic cells.

Zinc dissolves in dilute acids evolving hydrogen (except with nitric acid, p. 566) and forming zinc salts, and in hot alkali solutions evolving hydrogen and forming zincates: $Zn + 2OH' = ZnO_2'' + H_2$.

Brass.—Zinc when fused mixes with tin, copper and antimony, but only to a limited extent with lead or bismuth. Zinc and copper form definite compounds Zn_3Cu_2 and (probably) ZnCu, and two types of solid solutions called α- and β-brass. Brass with more than 64 p.c. copper is a homogeneous α-solution, that with 55–64 p.c. of copper is a mixture of α- and β-solutions.

The zinc increases the strength, toughness and hardness progressively up to 36 p.c., after which the increase in strength is more marked. Various alloys contain from 2 to 36 p.c. of zinc. *Gilding metal* (3–8Zn), *tombac* (gold colour: 10–18Zn), *pinchbeck* (dark gold colour, 7–11Zn), *cartridge brass* is 70Cu + 30Zn, *common brass* for sheets is 2Cu to 1Zn. All α-brasses are ductile and can be worked cold: tin, lead and aluminium are added for special purposes, *e.g.* alloy for condenser tubes contains 29Zn and 1Sn. The usual *casting brass* contains 27Zn, 2Pb and 1 Sn. *Muntz metal* is 60–62 Cu and 40–38 Zn. Brass with 1 5 to 2 p.c. of lead machines better; for free turning qualities 2 to 3 p.c. may be present. Manganese is added to 60 : 40 brass to increase the strength but often only traces are present in *manganese bronze*. A brass containing 2 p.c. of manganese takes a dark brown or chocolate colour when extruded hot, due to a film of oxide, and is used for window frames. *Aich metal* is 60Cu, 38Zn, and 2Fe; *Sterro metal* contains more iron. High tensile brasses contain nickel in place of some copper, *e.g.* 50Cu, 45Zn and 5Ni. If the zinc is kept at 45 the tensile strength increases up to 12 p.c. Ni. Alloys with 45 each of copper and zinc and 10 of nickel are white (*nickel brasses*) and can be worked hot.

Zinc Compounds

Zinc oxide ZnO, formed by burning zinc vapour in air, is called *zinc white* and used as a pigment. It is prepared for pharmaceutical purposes by precipitating zinc sulphate solution with sodium carbonate and heating the basic carbonate. It is a white powder which becomes sulphur-yellow on heating but white again on cooling, and there is no allotropic change. A hexagonal crystalline oxide is formed by the action of steam on red-hot zinc. Zinc oxide sublimes appreciably at 1400°. On exposure to air it takes up a little water

and carbon dioxide. Zinc oxide dissolves readily in dilute acids and also in alkalis, with which it forms *zincates*, *e.g.* solid $Na_2ZnO_2,4H_2O$.

A red form of zinc oxide, produced by fusing the white form with ammonium nitrate, contains 0·02 p.c. excess of zinc (Ehret and Greenstone, *J.A.C.S.*, 1943, **65**, 872).

Zinc oxide is used as a pigment, for polishing glass, as an absorbent in surgical dressings, as a filler for rubber and in making *Rinman's green*, which is obtained by heating zinc oxide with cobalt nitrate (as in the blowpipe test for zinc) and is a solid solution of cobalt zincate $CoZn_2O_3$ or $CoZnO_2$ in zinc oxide (Rinman, 1780; Hedvall, 1912–15).

Zinc hydroxide $Zn(OH)_2$ is formed as a white flocculent precipitate on adding alkali hydroxide or ammonia to a solution of a zinc salt. Ammonia does not precipitate it in presence of ammonium chloride (see p 365). The precipitate is soluble in excess of alkali hydroxide to form a zincate ion ZnO_2'', and in ammonia to form a complex ion $Zn(NH_3)_4^{··}$. Zinc hydroxide is amphoteric, as it also dissolves in acids to form zinc salts:

$$ZnO_2'' + 2H^{·} \rightleftharpoons Zn(OH)_2 \rightleftharpoons Zn^{··} + 2OH'.$$

Rhombic crystals of $Zn(OH)_2$ are deposited on slowly adding *N* $ZnSO_4$ solution to 50 c.c. of *N* KOH solution till a slight turbidity appears after shaking, and then allowing to stand (Goudriaan, 1920). Crystals are also formed when zinc turnings are immersed in contact with iron in ammonia solution.

A white or yellow impure hydrated **peroxide** ZnO_2 is formed by the action of 30 p.c. hydrogen peroxide on zinc oxide at −10° or by precipitating a solution of sodium zincate with 30 p.c. H_2O_2. It is used in surgery and dermatology (Foregger and Philipp, *J.S.C.I.*, 1906, **25**, 298).

Zinc halides have the following properties:

ZnF_2, tetragonal, m.p. 734°, volatile above 800°; $ZnF_2,4H_2O$ sparingly soluble.

$ZnCl_2$, hexagonal, m.p. 365° (Bassett and Bedwell, *J.C.S.*, 1931, 2485, give 313°), b.p. 730°, vapour density normal; hydrates with 4, 3, 2½, 1½ and $1H_2O$.

$ZnBr_2$, rhombic (?), m.p. 390°, b.p. *c.* 675°, hydrates with 3 and $2H_2O$.

ZnI_2, hexagonal, m.p. 450°, b.p. 624°, hydrate with $2H_2O$.

Fused zinc chloride, bromide and iodide are good electrolytes.

Zinc chloride $ZnCl_2$, discovered by Glauber in 1648 (*oil of calamine*), is formed by passing chlorine or hydrogen chloride over heated zinc, heating zinc with mercuric chloride: $Zn + HgCl_2 = ZnCl_2 + Hg$, heating zinc oxide at 700° in chlorine: $2ZnO + 2Cl_2 = 2ZnCl_2 + O_2$, heating zinc sulphate with sodium chloride, or heating $(NH_4)_3ZnCl_5$ in dry hydrogen chloride. It sublimes at a red heat in white hexagonal needles.

Zinc or the oxide, sulphide or carbonate dissolves in hydrochloric acid and the solution when evaporated to a syrup and mixed with a little concentrated hydrochloric acid deposits small deliquescent crystals of $ZnCl_2,H_2O$. If the solution is evaporated to dryness the **oxychlorides** Zn(OH)Cl and Zn_2OCl_2 are

formed to some extent, but if the dry mass is distilled at a red heat the anhydrous chloride passes over. By evaporation in a current of hydrogen chloride gas the fused salt is obtained and may be cast into sticks. It is very deliquescent and is soluble in alcohol, ether, acetone and pyridine. The mol. wt. is normal in quinoline and urethane but high in ether. An oxychloride formed by mixing the syrupy solution with zinc oxide sets rapidly to a very hard mass, used as a dental stopping. The concentrated solution of zinc chloride is used for impregnating timber to prevent " dry rot " and as a caustic (it dissolves proteins).

A solution of zinc chloride prepared by dissolving zinc in hydrochloric acid is used as a flux in soldering. On heating it liberates hydrochloric acid which dissolves metallic oxides and keeps the metal surface clean. Hot zinc chloride solution dissolves cellulose. Zinc chloride is used for " filling " (*i.e.* weighting) cotton goods.

Zinc chloride is only slightly hydrolysed (less than 0·1 p.c.). The transport number (p. 105) shows that complex ions, $ZnCl_3'$ or $ZnCl_4''$, are present in concentrated solutions.

Complex salts M^IZnCl_3 (M^I = Na, K, Rb, Cs, NH_4, $\frac{1}{2}$Ba, $\frac{1}{2}$Mg) are formed (and similar compounds from ZnF_2, $ZnBr_2$ and ZnI_2). The complex acids

$$H[ZnCl_3(H_2O)],H_2O \text{ and } H[Zn_2Cl_5],2H_2O$$

crystallise when hydrogen chloride gas is passed into a concentrated solution of zinc chloride in presence of zinc (Engel, 1886).

Zinc chloride forms $[Zn(NH_3)_4]Cl_2$ with ammonia gas and crystals of $[Zn(NH_3)_2]Cl_2$ separate in Leclanché batteries : the compounds are hydrolysed to basic salts by water but are soluble in dilute acid.

Zinc carbonate $ZnCO_3$ occurs as *calamine* or *smithsonite*, in rhombohedral crystals isomorphous with calcite. Sodium carbonate or bicarbonate precipitates white amorphous zinc carbonate which on standing under the mother-liquor forms $ZnCO_3,H_2O$. On washing this forms $2ZnCO_3,3Zn(OH)_2,H_2O$, the only basic carbonate (Mikusch, 1908). The carbonate or basic carbonate dissolves in concentrated potassium carbonate solution but is reprecipitated on dilution. A crystalline carbonate is formed by heating zinc sulphate solution with sodium bicarbonate in a sealed tube at 160°. Zinc carbonate (like zinc or zinc oxide) dissolves to some extent in water containing carbon dioxide, and zinc dissolves with effervescence in ammonium carbonate solution. Zinc carbonate begins to decompose at 140° and is rapidly decomposed at 300° : $ZnCO_3 = ZnO + CO_2$; when boiled with excess of sodium carbonate solution it forms zinc oxide.

Zinc on heating in nitrogen seems to form some nitride. Ammonia and a solution of zinc ethyl in dry ether give **zinc amide** $Zn(NH_2)_2$:

$$Zn(C_2H_5)_2 + 2NH_3 = Zn(NH_2)_2 + 2C_2H_6,$$

and on heating to dull redness this forms **zinc nitride** Zn_3N_2 :

$$3Zn(NH_2)_2 = Zn_3N_2 + 4NH_3,$$

a grey or green powder vigorously decomposed by water (Frankland 1858) :

$$Zn_3N_2 + 3H_2O = 3ZnO + 2NH_3.$$

Zinc nitrate $Zn(NO_3)_2,6H_2O$ is very deliquescent and is soluble in alcohol. There are hydrates with 9, 6, 5, 4, 3, 2 and $1\frac{1}{2}H_2O$. The anhydrous nitrate is formed by heating the tetrahydrate at 130°–135° in a current of carbon dioxide and N_2O_5 vapour: it decomposes at 140° (Markétos, 1912). Several basic nitrates are described.

Zinc phosphide Zn_3P_2 is a grey solid formed by heating zinc and phosphorus; it evolves phosphine with acids. **Zinc phosphate** $Zn_3(PO_4)_2,4H_2O$ occurs as the mineral *hopeite* and is obtained in pearly rhombic scales, insoluble in water but soluble in dilute acids and ammonia, by heating a solution of zinc sulphate and Na_2HPO_4. On heating it gives the anhydrous salt. The compounds $ZnHPO_4$, 1 and $3H_2O$, and $Zn(H_2PO_4)_2,2H_2O$ are also known (Eberly, Gross and Crowell, *J.A.C.S.*, 1920, **42**, 1433).

Zinc ammonium phosphate is precipitated like the magnesium salt (p. 367), but dissolves in excess of ammonia. When dried at 105° it is $ZnNH_4PO_4$ and may be weighed in the gravimetric determination of zinc, or gradually heated in an open crucible to form the white pyrophosphate $Zn_2P_2O_7$ (Finlay and Cumming, *J.C.S.*, 1913, **103**, 1004).

Zinc sulphide ZnS occurs as *blende* in cubic crystals and more rarely as *wurtzite* in hexagonal crystals. The transition temperature from blende to wurtzite is 1020°; the sulphide sublimes at 1180° and melts under pressure at about 1850°. Wurtzite may be formed from zinc vapour and hydrogen sulphide, and an artificial phosphorescent variety (*Sidot's blende*) formed on strongly heating the precipitated sulphide is used in making phosphorescent screens for X-ray and radioactivity work (MacDougal, Stewart and Wright, *J.C.S.*, 1917, **111**, 663). Massive zinc and sulphur do not react easily on heating, but the powders react with incandescence and the mixture may detonate on percussion. The sulphide is easily obtained by heating zinc oxide with sulphur and as a white precipitate on adding ammonium sulphide to a solution of a zinc salt; it is insoluble in excess but dissolves in all dilute mineral acids, but not in acetic acid (cf. MnS). The precipitate contains water which is removed only on strong heating. If hydrogen sulphide is passed through a solution of a zinc salt, zinc sulphide is at first precipitated, but owing to the acid formed the precipitation soon ceases (cf. Glixelli, *Z. anorg. Chem.*, 1907, **55**, 297): $Zn^{\cdot\cdot} + H_2S \rightleftharpoons ZnS + 2H^{\cdot}$. If sodium acetate is added the concentration of hydrogen ions is reduced and zinc sulphide is precipitated. If nickel and cobalt are present they are precipitated only after all the zinc has been deposited. The best conditions for precipitation of zinc sulphide are at 50°–100° in a solution buffered to pH 2 to 3 by ammonium sulphate and formate and formic acid (Fales and Ware, *J.A.C.S.*, 1919, **41**, 487).

Two modifications of zinc sulphide are precipitated, one (α-ZnS) in acid solution and another (β-ZnS) in alkaline solution, the second form having five times the solubility of the first. In acid solutions the precipitation of zinc sulphide shows a period of induction, which is longer the more acid is the solution. In some cases no precipitate is formed, although zinc sulphide is almost insoluble in the strength of acid used. Other sulphides, *e.g.* CuS and CdS, bring about simultaneous precipitation of the zinc sulphide.

Lithopone, a white pigment of good covering power and not blackened by hydrogen sulphide, is a mixture of zinc sulphide and barium sulphate made by precipitating zinc sulphate solution with barium sulphide and heating the precipitate: $ZnSO_4 + BaS = ZnS + BaSO_4$. Both zinc sulphide and lithopone darken on exposure to light owing to liberation of metallic zinc (Job and Emschwiller, 1923; Uehara, 1939–40).

Phosphorescence.—Reference has been made to the phosphorescence of calcium sulphide and nitrate, and barium and zinc sulphides. *Pure* compounds do not phosphoresce; the property is due to traces of heavy metals such as bismuth, lead, copper, manganese, molybdenum, tungsten, uranium, etc.

Phosphorescent calcium sulphide is obtained by heating a mixture of 100 parts of calcium carbonate with 30 parts of powdered sulphur for an hour to dull redness in a closed crucible. The mass is cooled and triturated with alcohol to which sufficient bismuth nitrate is added to give 1 part of bismuth to 10,000 of calcium sulphide. The mass is dried in the air and heated to dull redness for two hours. It is then slowly cooled.

Other phosphorescent masses are prepared by heating the mixtures *A* below (all weights in grams), powdering the product, moistening with the solutions *B*, and reheating at 900°–1000°:

1. *Violet light*: *A*: CaO (powder) 20, S 6, starch 2, Na_2SO_4 0·5, K_2SO_4 0·5. *B*: 2 c.c. of 0·5 p.c. $Bi(NO_3)_3$ solution + 0·5 c.c. of aqueous Tl_2SO_4.

2. *Deep blue light*: *A*: CaO 20, $Ba(OH)_2$ 20, S 6, K_2SO_4 1, Na_2SO_4 1, Li_2CO_3 2, starch 2. *B*: 2 c.c. of 0·5 p.c. alcoholic $Bi(NO_3)_3$ solution + 2 c.c. of 1 p.c. $RbNO_3$ solution.

3. *Bright green light*: *A*: $SrCO_3$ 40, S 6, Li_2CO_3 1, As_2S_3 1. *B*: 2 c.c. of 0·5 p.c. $TlNO_3$ solution.

4. *Deep orange-red light*: *A* (only): $BaCO_3$ 40, S 6, Li_2CO_3 1, Rb_2CO_3 0·47.

5. *Golden yellow light* (unusual) (Vanino and Schmid, *J. prakt. Chem.*, 1929, **124**, 52): $BaCO_3$ 25, $Sr(OH)_2$ 15, S 10, starch 3, Li_2SO_4 1, MgO 1, $Th(SO_4)_2$ 2 c.c. of 0·5 p.c. solution, $CuSO_4$ 3 c.c. of 0·4 p.c. solution. Heat 40 minutes.

Zinc sulphate $ZnSO_4,7H_2O$ (*white vitriol*), the commonest zinc salt, forms rhombic crystals isomorphous with Epsom salt $MgSO_4,7H_2O$. It is made by roasting blende at a moderate temperature or by dissolving the metal, oxide, sulphide or carbonate in dilute sulphuric acid, evaporating and crystallising below 39°. It is used in dyeing and calico-printing, making pigments and varnishes, and other zinc compounds, preserving wood and hides, fireproofing, and in pharmacy.

Between 39° and 70° the hydrate $ZnSO_4,6H_2O$ (monoclinic), and above 70° $ZnSO_4,H_2O$, is stable. At 280°, or lower in a current of dry air, anhydrous $ZnSO_4$ is formed, which at 767° decomposes to oxide: $ZnSO_4 = ZnO + SO_3$. Octahedral crystals of anhydrous salt are formed by heating a hydrate with ammonium sulphate (Klobb, 1892).

Zinc sulphate is freely soluble; the solubilities (g. $ZnSO_4$/100 g. H_2O) are:

	15°	30°	35°	39°
$ZnSO_4,7H_2O$ - -	50·88	61·92	66·61	70·05
$ZnSO_4,6H_2O$ - -	57·15	65·82	67·99	70·08

The solution is only slightly hydrolysed (0·03 p.c. in $\frac{1}{16}$ molar) and a $\frac{1}{8}$ p.c. solution is used as an eye lotion. Many double salts, *e.g.* $K_2Zn(SO_4)_2,6H_2O$, $MgZn(SO_4)_2,14H_2O$, etc., and a **basic sulphate** $[Zn\{Zn(OH)_2\}_3]SO_4$, are known.

Ammonia combines with many zinc salts to give ammines like those formed with copper, *e.g.* $Zn(NH_3)_4Cl_2,H_2O$, $Zn(NH_3)_4SO_4,H_2O$, $Zn(NH_3)_5SO_4$, etc.

Cadmium

Most zinc ores contain small amounts of cadmium, which also occurs as sulphide in the rare mineral *greenockite* CdS, hexagonal and isomorphous with wurtzite (ZnS). Blende may contain 2–3 p.c. of cadmium and calamine up to 5 p.c., but the average is less than 0·5 p.c.

A specimen of zinc oxide which was yellow although free from iron was found by Stromeyer in 1817 to contain the oxide of a new metal, to which he gave the name cadmium, from *cadmia*, the old name for zinc ore (*καδμεία*, in Dioskurides). Hermann showed that a yellow precipitate given by hydrogen sulphide from a solution of zinc oxide suspected to contain arsenic was cadmium sulphide.

Cadmium is more volatile than zinc, and the first portions of dust collecting in the receivers of zinc furnaces contain most of the cadmium in the form of the brown oxide CdO mixed with zinc oxide. The dust is heated at 850°–900° with coal in retorts with long sheet-iron adapter cones. The distillate may contain 20 p.c. or more of cadmium, whilst the original oxides contain only 1–6 p.c. The product is distilled with charcoal in small iron or clay retorts. In America much cadmium is extracted from lead and copper furnace fumes, and some from vat residues in electrolytic zinc-refining, from which it is precipitated by zinc.

Pure cadmium is tin-white, soft, s.g. 8·64 (cf. Lowry and Parker, *J.C.S.*, 1915, **107**, 1005), and " cries " like tin and zinc when bent. It has a low m.p. 321° and b.p. 767° and the vapour is monatomic. It oxidises only slowly in air, forming a transparent protective oxide coating, and a very thin (0·0002 in.) plating is used to protect iron and steel from rust ; it may be heat-treated so as to alloy with the iron.

Cadmium (1 p.c.) is alloyed with copper for overhead tramway wires, 0·5 p.c. is added to aluminium for casting, and it is added to silver to prevent staining as it is not affected by hydrogen sulphide. It is used in place of tin in some anti-friction alloys (*e.g.* with nickel) and in solders. Cadmium forms some fusible alloys, *e.g. Wood's metal*, m.p. 71°, is 1 Cd, 1 Sn, 2 Pb and 4 Bi. Cadmium amalgam is used in Weston cells and formerly as dental stopping, but it discolours the dentine. Cadmium forms a brown colloidal solution.

Cadmium dissolves slowly in dilute hydrochloric and sulphuric acids with evolution of hydrogen and readily in dilute nitric acid with evolution of oxides of nitrogen. The salts are usually colourless and are poisonous.

Cadmium halides are all volatile on heating; the solubility increases from the fluoride to the iodide:

CdF_2, cubic, m.p. 1100°, b.p. 1758°, sparingly soluble (4·5 g. in 100 g. H_2O at 25°), forms NH_4CdF_3.

$CdCl_2$, hexagonal, m.p. 568°, b.p. 964°, forms hydrates with 5 (?), 4, $2\frac{1}{2}$ (common), 2 (?) and $1H_2O$.

$CdBr_2$, hexagonal, m.p. 567°, b.p. 960°, very soluble, forms a hydrate with $4H_2O$.

CdI_2, hexagonal, m.p. 388°, b.p. 715°, very soluble, forms no hydrate.

Cadmium chloride $CdCl_2,2\frac{1}{2}H_2O$ is efflorescent; it is obtained anhydrous by heating in dry hydrogen chloride. **Cadmium iodide** CdI_2 forms white leaflets, also soluble in alcohol and acetone. The cadmium halides are only slightly ionised in solution and form complex ions (McBain, *Z. Elektrochem.*, 1905, **11**, 215), CdI_3' and CdI_4'': $2CdI_2 \rightleftharpoons Cd'' + CdI_4''$, hence cadmium hydroxide or sulphide is soluble in alkali iodide solution: $Cd(OH)_2 + 2I' = CdI_2 + 2OH'$. Complex cyanides, *e.g.* $K_2Cd(CN)_4$, are also easily formed, but as the instability constant of the complex ion $Cd(CN)_4''$ is relatively large, cadmium sulphide is precipitated from the cyanide solution by hydrogen sulphide (p. 171).

Cinnamon-brown **cadmium oxide** CdO (cubic) is formed on burning the metal in air or by heating the nitrate or carbonate; it volatilises at 700°. **Cadmium hydroxide** $Cd(OH)_2$ (hexagonal) is formed as a white precipitate on adding alkali hydroxide to a cadmium salt solution, preferably the nitrate. It is insoluble in excess of alkali but dissolves in ammonia to form the complex ion $Cd(NH_3)_4''$. Concentrated potassium iodide precipitates white $Cd(NH_3)_4I_2$ from the solution. Cadmium hydroxide is a strong base and absorbs carbon dioxide from the air; cadmium salts are not appreciably hydrolysed.

Cadmium carbonate $CdCO_3$ is precipitated in minute white hexagonal crystals on adding excess of ammonium carbonate to a solution of cadmium chloride, then ammonia till the precipitate just dissolves, and heating on a water bath. The precipitate with alkali carbonates is somewhat basic.

Cadmium nitrate $Cd(NO_3)_2,4H_2O$ (less commonly with $2H_2O$) is deliquescent and soluble in alcohol. An **amide** and **nitride** are formed as with zinc.

Cadmium sulphide is formed as a bright yellow precipitate on passing hydrogen sulphide into a not too acid solution of a cadmium salt. It crystallises in cubic and hexagonal forms (cf. ZnS), either of which may be yellow or red: in more acid solutions a red form (perhaps larger particles) precipitates (Egerton and Raleigh, *J.C.S.*, 1923, **123**, 3019; Milligan, *J. Phys. Chem.*, 1934, **38**, 797).

If the acid concentration exceeds 1·3 *N* the sulphide is not precipitated and it dissolves on boiling with dilute (1 : 5) sulphuric acid. According to Treadwell cadmium sulphide precipitated from the chloride always contains Cd_2SCl_2. Cadmium sulphide is an expensive yellow pigment; mixtures of sulphide and selenide are orange to deep red, and mixed with barium sulphate they form *cadmiopones* (cf. lithopone, p. 390).

Cadmium sulphate $CdSO_4$ forms hydrates with 7, $2\frac{2}{3}$ ($\frac{8}{3}$, the common hydrate), $2\frac{1}{2}$ and $1H_2O$; the monoclinic crystal hydrate $CdSO_4,\frac{8}{3}H_2O$ is used in the Weston cell (Perdue and Hulett, *J. Phys. Chem.*, 1911, **15**, 155). It forms double salts, *e.g.* $K_2Cd(SO_4)_2,6H_2O$.

The so-called "cadmous compounds" (Cd_2O, CdCl) are probably mixtures of bivalent cadmium compounds and finely divided metal (J. F. Spencer and Hollens, *J.C.S.*, 1934, 1062; 1935, 495).

Mercury

Mercury, the only metal truly liquid at ordinary temperature, is first mentioned by Aristotle (350 B.C.); he, and Theophrastos (300 B.C.), call it *liquid silver* (*chutos argyros*); Dioskurides (*c.* 50 A.D.) calls it *hydrargyros*. Pliny speaks of native mercury as quicksilver (*argentum vivum*, *i.e.* "live" silver), and the metal obtained by heating *cinnabar* (HgS, its important ore) as *hydrargyrum* (liquid silver), and he says it was used in the extraction of gold.

Mercury was only admitted to be a true metal when frozen to a malleable solid (m.p. $-38{\cdot}9°$) by Braune in 1759; the freezing of a mercury thermometer was noticed in Siberia in 1736.

Small quantities of mercury occur native or as amalgams and halogen compounds, but the only important ore is *cinnabar*, mercuric sulphide HgS, a red or black mineral found in Almaden (Spain), Idria (Carniola), Monte Amiata (Italy), and in smaller amounts in Russia, the U.S.A., Mexico, Central China, and Japan. In the extraction of the metal the ore (which may contain only 0·5–1 p.c. of HgS) is roasted in a current of air: $HgS + O_2 = Hg + SO_2$.

In the older process, now used only at Almaden, the ore rests on a perforated arch in a shaft and is heated in a current of air. The vapours pass into a series of stoneware receivers called *aludels*, from which the condensed mercury flows through a channel into cisterns. The metal is exported in iron bottles holding about 75 lb.

In modern processes, lump ore is roasted with charcoal in shaft furnaces, and the mercury vapour condensed in earthenware pipes cooled in water (Fig. 186); and powdered ore in furnaces containing

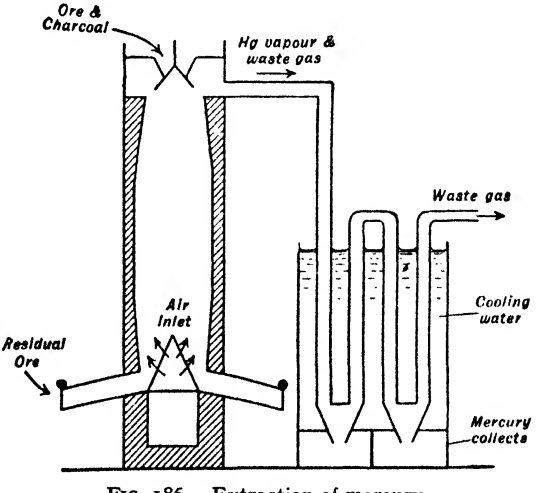


FIG. 186.—Extraction of mercury.

shelves sloping alternately in opposite directions, down which the ore slides and flames and air pass upwards. Rich ores, and flue dust from the furnaces, are distilled in iron retorts with quicklime or iron filings :

$$4HgS + 4CaO = 4Hg + 3CaS + CaSO_4$$
$$HgS + Fe = FeS + Hg.$$

Commercial mercury usually contains lead, copper, etc. It leaves a " tail " when run over a glass surface and forms a black scum of oxides when shaken with air. It is *purified* by running it several times in a thin stream through 5 p.c. nitric acid containing a little mercurous nitrate in a glass tube 1·3 m. long and 3 cm. wide (Fig. 187). Another good method is to shake with a con-

FIG. 187.—Purification of mercury.

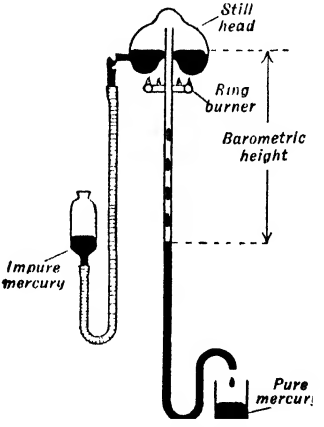


FIG. 188.—Mercury still.

centrated solution of potassium permanganate in $6N$ H_2SO_4 containing a little ferric chloride (Russell and Evans, *J.C.S.*, 1925, **127**, 2221). The metal is then distilled in a vacuum with a still surface of the mercury (Fig. 188) (if it bumps, impurities are carried over) or in a slow stream of filtered air (Hulett, *Phys. Rev.*, 1905, **21**, 288 ; 1911, **33**, 307).

Mercury is a silver-white liquid metal, s.g. 13·5955 at 0°. It has a high surface tension and easily forms spherical drops, *e.g.* on a glass plate. The m.p. is −38·90° ; at −185° the s.g. of the solid is 14·383. The b.p. is 356·95° and the vapour is monatomic (some Hg_2 molecules are detected spectroscopically). The liquid in very thin films transmits blue light. A brown colloidal solution is formed, *e.g.* by reducing mercuric nitrate solution with hydrazine, but is stable only in presence of protective colloids. Mercury is " killed " or converted into a grey powder when ground with fats or powders such as sugar : the globules may be as small as 0·002 mm. diameter.

Mercury has a very small vapour pressure at room temperature (< 0·0002 mm. at 0°; 0·008 mm. at 40°; 0·270 mm. at 100°), but in laboratory air it becomes covered with an oily film and is practically non-volatile. *The vapour is very poisonous*, and the metal should never be heated whilst exposed to the air of the laboratory.

Mercury combines with chlorine and bromine at room temperature, with iodine when ground in a mortar, and with oxygen and sulphur on heating (ozone oxidises it at room temperature; p. 664). It is not attacked in absence of air by cold or hot dilute hydrochloric acid, by cold concentrated hydrochloric or dilute sulphuric acid, or by alkalis. It dissolves easily in dilute nitric acid and in aqua regia, and forms mercuric sulphate with hot concentrated sulphuric acid. It is attacked by gaseous hydrogen iodide in the cold, forming mercurous and mercuric iodides.

Mercury dissolves many metals, forming amalgams. Many contain definite compounds, *e.g.* $NaHg_2$, KHg_2, Au_2Hg, MgHg, etc.

Iron is not easily amalgamated but an amalgam is formed by triturating iron powder with mercuric chloride and water. Mercury readily penetrates sheet copper, rendering it brittle. Copper amalgam becomes plastic when warmed to 100° and rubbed in a mortar. After ten to twelve hours it again becomes hard. It is used for stopping teeth. Another dental amalgam is made by adding mercury to a silver-tin alloy Ag_3Sn, and the plastic mass hardens to a non-tarnishing mass because of the reaction:

$$5Ag_3Sn + 24Hg = 3Ag_5Hg_8 + 5Sn.$$

EXPT. 1.—Pour a little mercury into a solution of silver nitrate. A tree-like growth (*arbor Dianae*) of silver amalgam is produced.

The two series of mercury compounds both contain bivalent mercury, the **mercuric compounds** $=Hg$ and the **mercurous compounds** $—Hg—Hg—$ or $=Hg_2$. The corresponding ions are $Hg^{\cdot\cdot}$ and $Hg_2^{\cdot\cdot}$ (Ogg, 1898). In halogen compounds, however, mercury is covalent. The mercurous compounds are often formulated for simplicity as HgX instead of Hg_2X

MERCUROUS COMPOUNDS

Most mercurous compounds (the fluoride and nitrate are exceptional) are sparingly soluble and not easily hydrolysed, and they show little tendency to form complex ions.

The **halides** are crystalline solids:

Hg_2F_2, cubic, yellow, m.p. 570°.

Hg_2Br_2, tetragonal, yellowish-white, s.g. 7·3, sublimes 350°, m.p. 405°.

Hg_2Cl_2, tetragonal, white, s.g. 7·15, m.p. 302°, b.p. 383·7°.

Hg_2I_2, tetragonal, yellow, s.g. 7·7, sublimes 140°, m.p. (decomp.) 290°.

The structure of mercurous halides Hg_2X_2 (X = Cl, Br, I) has been established by X-ray analysis (Maugin, 1924; Havinghurst, *J.A.C.S.*, 1926, **48**, 2113):

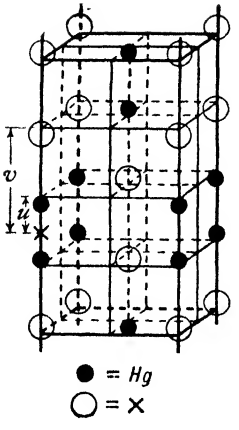


FIG. 189.—Structure of mercurous halides.

the unit cell is tetragonal and contains two Hg_2X_2 molecules (Fig. 189).

Mercurous fluoride Hg_2F_2 is soluble, but the other halides are insoluble. It separates in small crystals from a solution of mercurous carbonate in aqueous hydrofluoric acid.

Mercurous chloride (*calomel*) Hg_2Cl_2 was known early in China and Japan (Divers, *J.S.C.I.*, 1894, **13**, 108). It is formed as a white precipitate on adding mercurous nitrate solution to excess of hot sodium chloride solution, but is usually made for medicinal use as a purgative by subliming a mixture of mercuric chloride and metallic mercury (made by grinding the substances in a mortar) in an iron pot. The crust of calomel subliming on the lid is ground, and boiled with water (to remove the very poisonous mercuric chloride, some of which sublimes). The powder consists of white needles. It is sparingly soluble in water (0·4 mg. per lit. at 20°) but dissolves in hot concentrated nitric acid :

$$3Hg_2Cl_2 + 8HNO_3 = 3HgCl_2 + 3Hg(NO_3)_2 + 2NO + 4H_2O,$$

and in concentrated hydrochloric acid with deposition of mercury :

$$Hg_2Cl_2 + HCl = Hg + HHgCl_3, \text{ and } HHgCl_3 + HCl = H_2HgCl_4 ;$$

the solution contains the ions $HgCl_3'$ and $HgCl_4''$.

The nature of calomel vapour has been disputed (cf. Smith and Menzies, *J.A.C.S.*, 1910, **32**, 1541). Odling (*J.C.S.*, 1864, **17**, 221) showed that it amalgamated gold-leaf and hence assumed the presence of free mercury vapour formed by dissociation : $Hg_2Cl_2 = Hg + HgCl_2$. The vapour density corresponds with complete dissociation but would also agree with HgCl ; Harris and Victor Meyer (1894) showed that in a porous earthenware tube mercury diffuses out and condenses on a cold surface and the residue in the tube contains excess of $HgCl_2$. H. B. Baker (*J.C.S.*, 1900, **77**, 646) found that the vapour density of very dry calomel corresponds with Hg_2Cl_2 and the vapour does not amalgamate gold-leaf, and this formula was found by Beckmann (1907) from the freezing point depression in fused mercuric chloride. Gucker and Munch (*J.A.C.S.*, 1937, **59**, 1275), however, found the density of the dry vapour to correspond with $Hg + HgCl_2$ or HgCl, and since the vapour is diamagnetic, HgCl (which has an odd electron) is excluded (Selwood and Preckel, *J.A.C.S.*, 1940, **62**, 3055). Both solid and fused calomel conduct electricity.

Mercurous iodide Hg_2I_2 is formed as a yellow crystalline precipitate on adding concentrated potassium iodide solution to dilute mercurous nitrate solution acidified with nitric acid, and as a green powder by grinding 10 g. of mercury and 6·35 g. of iodine in a dry mortar. The pure iodide is formed by boiling excess of iodine with mercurous nitrate solution containing a little nitric acid and cooling, when transparent yellow crystals separate : these blacken on exposure to light, probably from the reaction $Hg_2I_2 = Hg + HgI_2$.

Mercurous oxide Hg_2O is formed as a black powder by precipitating mercurous nitrate solution with sodium hydroxide or grinding calomel with sodium hydroxide solution. It decomposes at 100° or on exposure to light (slowly in the dark) into yellow mercuric oxide and mercury: $Hg_2O = HgO + Hg$, and the product always contains some free mercury. There is some chemical evidence for the existence of Hg_2O, *e.g.* it dissolves completely in acetic acid (Barfoed, 1888; Hada, *J.C.S.*, 1896, **69**, 1667; von Antropoff, 1908), but the X-ray spectrum shows only lines of Hg and HgO (Fricke and Ackermann, 1933).

Mercurous carbonate Hg_2CO_3 is precipitated as a yellow powder on adding excess of potassium bicarbonate solution to mercurous nitrate solution and allowing to stand for a few days to decompose any basic nitrate. It decomposes at 130° or on exposure to light: $Hg_2CO_3 = HgO + Hg + CO_2$.

Mercurous nitrate is formed in colourless monoclinic crystals $Hg_2(NO_3)_2$, $2H_2O$ by the action of cold dilute nitric acid on excess of mercury (Ray, *J.C.S.*, 1897, **71**, 337; 1905, **87**, 171). It decomposes on heating: $Hg_2(NO_3)_2 = 2HgO + 2NO_2$. With water it gives a white precipitate of basic nitrate which dissolves in dilute nitric acid. The solution is kept in contact with mercury to prevent oxidation to mercuric nitrate. A crystalline basic nitrate (*Marignac's salt*) is $3Hg_2(NO_3)_2,2Hg_2O,2H_2O$ or $Hg_5(NO_3)_3(OH)_2$.

Mercurous sulphide Hg_2S is formed by the action of carbon dioxide and hydrogen sulphide on dry mercurous chloride at −10° (Antony and Sestini, 1894). The precipitate from mercurous nitrate solution by H_2S is a mixture of HgS and finely divided mercury.

Mercurous sulphate Hg_2SO_4 is formed by warming excess of mercury with concentrated sulphuric acid (or with fuming acid in the cold), and deposits on cooling as a coarse crystalline (monoclinic) powder. It is formed as a white precipitate (solubility 0·6 g. per lit. at 25°) by adding mercurous nitrate solution to dilute sulphuric acid. When excess of acid is removed by washing, hydrolysis begins, and with water at 25° a greenish-yellow basic salt Hg_2SO_4,Hg_2O,H_2O is formed. According to Hulett (1904) the pure sulphate is best obtained by electrolysis with a mercury anode in dilute sulphuric acid (1 to 6 by volume) and a current density of 0·5 amp. per sq. cm. Mercurous sulphate is used as a depolariser in the Weston cell.

Mercuric Compounds

The mercuric compounds HgX_2 are formed by oxidation of the mercurous compounds Hg_2X_2, and are easily reduced to mercurous compounds or metallic mercury.

Mercurous chloride is precipitated by sulphur dioxide from mercuric chloride solution: $2HgCl_2 + 2H_2O + SO_2 = Hg_2Cl_2 + 2HCl + H_2SO_4$, and stannous chloride precipitates white mercurous chloride, or grey mercury if in excess:

$$2HgCl_2 + SnCl_2 = Hg_2Cl_2 + SnCl_4$$
$$Hg_2Cl_2 + SnCl_2 = 2Hg + SnCl_4.$$

All mercury compounds are reduced to the metal if boiled with hydrochloric acid and copper foil, which becomes white owing to amalgamation, and on heating the foil in a glass tube a sublimate of minute globules of mercury is formed. A similar sublimate is obtained if a mercury salt is heated with powdered charcoal and sodium carbonate.

The mercuric halides are only slightly ionised and the oxy-salts tend to hydrolyse and form basic salts. Mercuric compounds show a marked tendency to form complex anions.

Mercuric oxide HgO is slowly formed as a heavy *red* crystalline (rhombic) powder (*red precipitate*) on heating mercury in air at about 300° in an open flask with a long neck. The reaction is reversible : $2Hg + O_2 \rightleftharpoons 2HgO$, and at higher temperatures the oxide decomposes. If the mercury is prevented from condensing an equilibrium is set up. The crystalline red oxide is also formed by heating at a moderate temperature mercuric nitrate or a mixture of this and mercury :

$$2Hg(NO_3)_2 = 2HgO + 4NO_2 + O_2 \text{ and } Hg(NO_3)_2 + Hg = 2HgO + 2NO_2.$$

A *yellow* precipitate of mercuric oxide is formed by adding a solution of mercuric nitrate to a solution of alkali hydroxide. According to Gay-Lussac (1843) and Ostwald (1895, 1900) the red and yellow forms differ only in the finer division of the yellow : the red form becomes yellow on grinding, and on precipitation from hot solutions the colour is orange. Schoch (1903) believed the two varieties to have different crystalline forms, solubilities (yellow 0·0520, red 0·0515 g./lit. at 25°) and dissociation pressures at 300°. Both forms, however, are rhombic, and Taylor and Hulett (*J. Phys. Chem.*, 1913, **17**, 565) found the dissociation pressures identical. Mercuric oxide is more soluble in alkali solution than in water (Fuseya, *J.A.C.S.*, 1920, **42**, 368). It is reduced by hydrogen below 225°.

Mercury peroxide HgO_2 is obtained as an amorphous brick-red powder when hydrogen peroxide and alcoholic potash are added to a solution of mercuric chloride in alcohol. It is fairly stable but is decomposed by water. The peroxide is formed by the action of hydrogen peroxide on mercuric oxide at 0°, but decomposes with evolution of oxygen, leaving finely divided mercury.

Mercuric Halides

HgF_2, white, octahedral, m.p. 645°, b.p. 650°.

$HgCl_2$, white, rhombic, m.p. 277°, b.p. 303°.

$HgBr_2$, white, rhombic, m.p. 235°, b.p. 325°.

HgI_2, red tetragonal, yellow rhombic, m.p. 255°, b.p. 351°.

Mercuric fluoride HgF_2 is formed by heating mercurous fluoride in dry chlorine at 275° or alone in vacuum at 450°. It is hydrolysed and discoloured by traces of moisture. The hydrate $HgF_2,2H_2O$ separates in white crystals from a solution of mercuric oxide in excess of hydrofluoric acid ; it is easily hydrolysed to a yellow basic salt Hg(OH)F. Double fluorides with alkali fluorides do not seem to be formed.

Mercuric chloride (*corrosive sublimate*) is rapidly formed by the action of chlorine on mercury, even if the substances are quite dry, a white crust forming on the metal: $Hg + Cl_2 = HgCl_2$. The action is more rapid on heating and mercuric chloride is now made technically in this way.

In an older process (Kunckel, 1716) mercuric sulphate made by evaporating mercury and concentrated sulphuric acid to dryness was mixed with an equal weight of sodium chloride and a little manganese dioxide (to prevent the formation of mercurous chloride from some mercurous sulphate in the mercuric sulphate) and sublimed in a long-necked flat-bottomed flask on a sand bath:

$$HgSO_4 + 2NaCl = HgCl_2 + Na_2SO_4.$$

The flask was cooled and broken to extract the cake of sublimate.

Mercuric chloride is colourless, s.g. 5·41, crystallises by sublimation and from solution in rhombic needles, sparingly soluble in cold but readily in hot water (4·3 g./100 g. H_2O at 0°, 6·57 at 10°, 54 at 100°). It is a violent poison, 0·2–0·4 g. being fatal: the antidote is an immediate administration of white of egg followed by an emetic. It is used as a bactericide, in preserving skins and in 0·1 p.c. solution for sterilising surgical instruments: the action is strongest in feebly alkaline solutions (pH 5 to 6·6). The solution is slightly hydrolysed but is practically unionised (as mercuric chloride is covalent) and contains polymerised molecules (Bourion and Rouyer, 1923).

The solid is not decomposed either by hot concentrated sulphuric acid (when it sublimes unchanged) or by nitric acid. Mercuric chloride is readily soluble in alcohol and in ether (which extracts it from solution in water).

The solution of mercuric chloride contains the complex ions $HgCl^+$, $HgCl_3'$ and $HgCl_4''$. The solid dissolves with evolution of heat in concentrated hydrochloric acid; the solution does not fume and on cooling deposits crystals of **chloromercuric acid** $HHgCl_3$. With chlorides of alkali-metals crystalline compounds are formed, *e.g.* $KHgCl_3$ and Na_2HgCl_4, which are partly decomposed in solution and partly ionised into complex ions: $Na_2HgCl_4 = 2Na^+ + HgCl_4''$. A solution of Na_2HgCl_4 is used instead of $HgCl_2$ as an antiseptic, since it is neutral in reaction and does not coagulate proteins. The ammonium salt $(NH_4)_2HgCl_4.H_2O$ was called *sal alembroth*.

Alkalis precipitate mercuric chloride incompletely and mercuric oxide dissolves in hot solutions of alkali-chlorides forming strongly alkaline liquids: $HgCl_2 + 2OH' \rightleftharpoons HgO + 2Cl' + H_2O$. The concentration of mercuric ions from the dissociation of mercuric chloride is less than that in the saturated solution of mercuric oxide.

Mercuric oxychlorides, *e.g.* $2HgCl_2.HgO$ (red), $HgCl_2.2HgO$ (black), $HgCl_2.3HgO$ (yellow) and $HgCl_2.4HgO$ (black) are formed by boiling mercuric oxide with mercuric chloride solution.

Mercuric bromide $HgBr_2$ is similar to the chloride but less soluble (Garrett, *J.A.C.S.*, 1939, **61**, 2744).

Mercuric iodide HgI_2 is formed as a yellow precipitate which rapidly becomes scarlet (the change is slower in presence of gelatin: Friend, *Nature*, 1922, **109**, 341) on adding the calculated amount of potassium iodide solution to mercuric

chloride solution, and as a red solid by grinding mercury with the correct amount of iodine (Courtois, 1813), with or without a little alcohol, or by adding ethyl iodide to a solution of mercuric chloride. At 127°–128° the red tetragonal form is converted into a yellow rhombic form (first deposited from solution or by sublimation); the reverse change occurs on cooling, but the yellow form may persist unless the solid is rubbed. On cooling in liquid air the red form becomes yellow, and the yellow form white. Another very labile white form is deposited by heating at 300°–500° and cooling the vapour under reduced pressure (Tammann, 1920).

Mercuric iodide is very sparingly soluble in water (not more than 0·06 g./lit. at 25°) but more soluble in alcohol, and on pouring the alcoholic solution into water the yellow form, which persists for some time, is precipitated.

It is readily soluble in mercuric chloride or potassium iodide solution. A solid complex compound **potassium mercuri-iodide** $KHgI_3$ (or $KHgI_3,H_2O$) is formed (Dunningham, *J.C.S.*, 1914, **105**, 364, 724; Pernot, *Ann. Chim.*, 1931, **15**, 5) and the solution contains the ion HgI_3' and possibly HgI_4'' (Sherrill, *Z. phys. Chem.*, 1903, **43**, 705; Garrett, *J.A.C.S.*, 1939, **61**, 2744). The solution is not precipitated by bases, since practically no mercuric ions are present, and mercuric oxide dissolves in a solution of potassium iodide to form a strongly alkaline liquid: $HgO + 3I' + H_2O = HgI_3' + 2OH'$.

A solution of potassium mercuri-iodide containing excess of caustic potash is **Nessler's reagent.** With traces of ammonia a brown colour, with larger amounts a brown precipitate, is formed; the composition of this was given as NHg_2I,H_2O, but it is said to be $NH_2Hg_2I_3$ (Nichols and Willits, *J.A.C.S.*, 1934, **56**, 769).

Mercuric carbonate is known only as two basic salts, ochre-yellow $HgCO_3,2HgO$ and brown $HgCO_3,3HgO$, formed on adding mercuric nitrate solution to a large excess of $KHCO_3$ and K_2CO_3 solution, respectively.

Mercuric nitrate is obtained with difficulty in large very deliquescent crystals $Hg(NO_3)_2,\frac{1}{2}H_2O$ (Millon) or $Hg(NO_3)_2,H_2O$ (Cox) by dissolving mercury in excess of hot concentrated nitric acid and evaporating over quicklime in a desiccator. The mother-liquor on evaporation deposits a basic salt and $Hg(NO_3)_2,2HgO$ deposits as a white powder by the action of water on the nitrate at 25° (Cox, *Z. anorg Chem.*, 1904, **40**, 146); it is decomposed into mercuric oxide by excess of water. Mercuric nitrate is precipitated from solution by concentrated nitric acid.

By adding a solution of HgI_2 in liquid ammonia to an excess of potassamide KNH_2 dissolved in liquid ammonia, a chocolate-brown precipitate of **mercuric nitride** Hg_3N_2 is formed. **Mercuric cyanide** $Hg(CN)_2$ is only slightly ionised and is formed by dissolving HgO in aqueous HCN and crystallising; it is used in the preparation of cyanogen: $Hg(CN)_2 = Hg + C_2N_2$. The **thiocyanate** $Hg(CNS)_2$ is formed as a white precipitate on adding KCNS to $Hg(NO_3)_2$ solution; when made into small pills with gum tragacanth soaked in water, and lit with a taper it gives a long, snake-like mass of a polymerised cyanogen product (*Pharaoh's serpent*). **Mercuric fulminate** $Hg(ONC)_2$ is formed as a white precipitate by warming a solution of mercuric nitrate and excess of nitric acid with alcohol.

Mercuric sulphide HgS occurs as *cinnabar* and is the red pigment *vermilion*, which blackens on exposure to light. It is formed by grinding mercury and sulphur with a little caustic potash solution. The black amorphous sulphide first formed slowly becomes red and crystalline. Black mercuric sulphide is precipitated by hydrogen sulphide from a solution of a mercuric compound: $HgCl_2 + H_2S = HgS + 2HCl$.

The black precipitate of HgS first formed becomes white if shaken with excess of mercuric chloride solution, $Hg(HgS)_2Cl_2$ being produced. The further action of H_2S changes this into a red and finally a black precipitate (HgS). The black precipitate becomes red on sublimation. It is insoluble in boiling hydrochloric acid (unless very concentrated) or dilute nitric acid, but dissolves in hydrobromic and hydriodic acids, evolving H_2S, and in aqua regia (when the sulphur mostly separates). Mercuric sulphide dissolves in concentrated alkali sulphides, forming thio-salts, *e.g.* $K_2HgS_2,5H_2O$ (white needles). It is readily soluble in a mixture of sodium hydroxide and ammonium sulphide and in sodium hydroxide alone if As, Sb and Sn are present (Walker, *J.C.S.*, 1903, **83**, 184). Boiling concentrated sulphuric acid forms $HgSO_4$: $HgS + 2H_2SO_4 = HgSO_4 + SO_2 + S + 2H_2O$. It burns when heated in air: $HgS + O_2 = Hg + SO_2$, and is decomposed when heated with iron filings or quicklime (p. 394).

The red crystalline form is less soluble in alkali sulphides than the black amorphous form; the latter is slowly converted into scarlet vermilion when digested with sodium sulphide solution.

There are two *crystalline* forms of mercuric sulphide: (i) red hexagonal *cinnabar*, s.g. 8·176, stable below 380°, and (ii) black cubic *metacinnabar*, s.g. 7·60, stable above 380°, and rarely found native (Allen and Crenshaw, 1912; Kolkmeijer, 1924; Rinse, 1928).

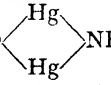
Mercuric sulphate $HgSO_4$ is obtained by boiling mercury with one and a half times its weight of concentrated sulphuric acid and evaporating to dryness: $Hg + 2H_2SO_4 = HgSO_4 + SO_2 + 2H_2O$. The white residue may be crystallised (rhombic) from sulphuric acid. Mercuric sulphate is very hygroscopic. With a small quantity of water it forms colourless crystals of $HgSO_4,H_2O$ but with more water it hydrolyses at 25° forming a yellow crystalline sparingly soluble powder of the basic sulphate $3HgO,SO_3$ or $HgSO_4,2HgO$, formerly called *turpeth mineral*. Mercuric sulphate decomposes at 400°: $3HgSO_4 = Hg_2SO_4 + Hg + 2SO_2 + 2O_2$, and a current of hydrogen chloride converts it quantitatively into mercuric chloride.

Mercurammine compounds.—As compared with other elements of the group mercury shows a marked tendency to form *basic salts, complex compounds* (especially of the mercuric halides) and *ammines*.

Mercuric chloride absorbs ammonia gas to form $HgCl_2,2NH_3$, called *fusible white precipitate*, also formed as a white precipitate on adding mercuric chloride solution to a boiling solution of ammonium chloride and ammonia. It was formerly regarded as mercuri-diammonium chloride $Hg(NH_3Cl)_2$, but is probably a coordination compound $[Hg(NH_3)_2]Cl_2$. A compound $3HgCl_2,2NH_3$ is also known (Holmes, *J.C.S.*, 1918, **113**, 74).

Ammonia solution does not precipitate mercuric oxide from a solution of mercuric chloride but gives a white precipitate of **aminomercuric chloride** $NH_2{\cdot}HgCl$,

i.e. mercuric chloride in which one atom of chlorine is replaced by NH_2. This is called *infusible white precipitate.*

If mercuric oxide is gently warmed with aqueous ammonia, a yellow powder known as **Millon's base** is formed. According to Rammelsberg (1888) this is dimercurammonium hydroxide $NHg_2OH,2H_2O$. On drying in ammonia gas at 125° the dark brown explosive NHg_2OH or perhaps  is formed.

The brown precipitate obtained by the action of ammonia on Nessler solution was formerly regarded as NHg_2I,H_2O. Hofmann and Marburg (1899) formulated Millon's base as $(HOHg)_2NH_2{\cdot}OH$, but the formula $HO{\cdot}(Hg_2O){\cdot}NH_2,H_2O$ is now usually adopted, since the compound loses H_2O when dried in ammonia gas and forms $NH_2{\cdot}Hg{\cdot}O{\cdot}Hg{\cdot}OH$. Compounds isomeric with salts of Millon's base were prepared by Franklin (1905, 1912) by the action of liquid ammonia on $HgBr_2$ and HgI_2; he formulated them as $Hg{:}N{\cdot}HgX$ and Millon's base as

$$HO{\cdot}Hg{\cdot}NH{\cdot}Hg{\cdot}OH.$$

Holmes recognised three classes of mercuri-ammine compounds: (i) co-ordination compounds such as $[Hg(NH_3)_2]Cl_2$, (ii) ammonolysed compounds in which NH_2, NH or N is substituted for part of the acid radical, *e.g.* $Cl{\cdot}Hg{\cdot}NH_2$, (iii) ammonolysed and hydrolysed compounds, *e.g.* the chloride of Millon's base $NH_2{\cdot}Hg{\cdot}O{\cdot}Hg{\cdot}Cl$, formed by heating infusible white precipitate with a large amount of water for twelve hours at 60°–70°, when hydrolysis occurs:

$$2NH_2{\cdot}Hg{\cdot}Cl + H_2O = NH_2{\cdot}Hg{\cdot}O{\cdot}Hg{\cdot}Cl + NH_4Cl.$$

Infusible white precipitate contains an NH_2 group and has chlorine directly attached to mercury, as is proved by the reactions: (i) a monoethylamine compound $NH(C_2H_5){\cdot}Hg{\cdot}Cl$ is formed by the action of ethylamine $NH_2(C_2H_5)$ on $HgCl_2$, (ii) hydrofluoric acid converts infusible white precipitate into HgF_2, $HgCl_2$ and NH_4F, (iii) platinic chloride forms with it a yellow crystalline compound: $NH_2{\cdot}Hg{\cdot}Cl,PtCl_4$ or $Hg[PtCl_5(NH_2)]$, (iv) infusible white precipitate is formed by the action of sodamide on $HgCl_2$: $NaNH_2 + HgCl_2 = NaCl + NH_2{\cdot}Hg{\cdot}Cl$.

Only *mercuric* compounds form ammines with ammonia; *mercurous* compounds are decomposed into mercuric compounds and mercury. Aqueous ammonia forms with calomel (Hg_2Cl_2) a black powder which is a mixture of infusible white precipitate and finely divided mercury (Barfoed, 1889), $Hg + NH_2{\cdot}Hg{\cdot}Cl$. In ordinary conditions the precipitate [ ] contains mercurous oxide (Freche and Sneed, *J.A.C.S.*, 1938, **60**, 518):

$$2Hg_2Cl_2 + 4NH_4OH = [Hg + Hg_2O + NH_2{\cdot}Hg{\cdot}Cl] + 3NH_4Cl + 3H_2O.$$

(This reaction is said to be the origin of the name calomel, from the Greek *kalos* beautiful, and *melas* black). A similar black precipitate containing mercury and $NH_2{\cdot}Hg{\cdot}NO_3$ is formed with ammonia and mercurous nitrate solution. The mineral *kleinite*, once supposed to be mercuric oxychloride, is said to be mostly NHg_2Cl (Hillebrand, 1906–07).

CHAPTER XVI

GROUP III OF THE PERIODIC SYSTEM

Group III of the periodic system is in two parts :

The (a) Sub-group : metals of the rare earths and the radioactive element actinium (p. 203).

The densities at room temperature and the lattice types of the rare earth elements (Klemm and Bommer, *Z. anorg. Chem.*, 1937, **231**, 138 ; values for Sc and Sm from older data) and the approximate m.ps., when known, are given below (c.p. = close packed ; f.c. = face-centred ; b.c. = body-centred) :

At. no.	Lattice	Density	At. vol.	M.p.	At. no.	Lattice	Density	At. vol.
21 Sc	—	2·5 (?)	18·0	1200°	64 Gd	hexag. c.p.	7·95	19·7
39 Y	hexag. c.p.	4·34	20·5	1475°	65 Tb	hexag. c.p.	8·33	19·1
57 La-α	hexag. c.p.	6·19	22·5	810°	66 Dy	hexag. c.p.	8·56	18·9
57 La-β	cubic f.c.	6·18	—	—	67 Ho	—	—	—
58 Ce-α	hexag. c.p.	6·78	23·2	630°	68 Er	hexag. c.p.	9·16	18·2
58 Ce-β	cubic f.c.	6·81	—	—	69 Tm	hexag. c.p.	9·35	18·1
59 Pr-α	hexag. c.p.	6·78	20·8	940°	70 Yb	cubic f.c.	7·01	24·7
59 Pr-β	cubic f.c.	6·81	—	—	71 Lu	hexag. c.p.	9·74	18·0
60 Nd	hexag. c.p.	7·00	20·6	840°				
61 —	—	—	—	—				
62 Sm	—	7·7	20·0	1350°				
63 Eu	cubic b.c.	5·24	31·9	—				

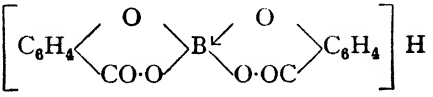
The abnormally high atomic volumes of europium and ytterbium are noteworthy. The electron configurations of the atoms are given on p. 435.

The (b) Sub-group : boron, aluminium, gallium, indium and thallium.

	B	Al	Ga	In	Tl
Atomic number	5	13	31	49	81
Electron configuration	2·3	2·8·3	2·8·18·3	2·8·18·18·3	2·8·18·32·18·3
Density	2·34	2·70	5·9	7·31	11·85
Atomic volume	4·62	10·0	11·8	15·1	17·2
Melting point	2300°	659·8°	29·75°	155·4°	303·5°
Boiling point	2550°	>2200°	>2000°	>1450°	1475°

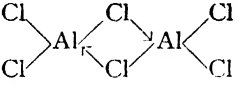
The typical group valency is 3 but boron forms several volatile hydrides in which its valency is anomalous ; some metals of the rare earths (Sm, Eu, Yb) can be bivalent as well as tervalent, and in many of its stable compounds cerium is quadrivalent, as is praseodymium in the oxide PrO_2 ; gallium and indium also form compounds in which they are uni- and (possibly) bivalent, and thallium is most stable in its univalent compounds. Boron shows many analogies with carbon and especially with silicon, in Group IV.

The maximum covalency of boron (in a short period) is 4 and this is shown in many compounds, *e.g.* KBF_4. The valency arrangement is tetrahedral in such compounds as borosalicylic acid :

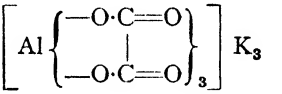


which show optical isomerism (Böseken, 1926).

Aluminium shows a covalency of 4 in the bimolecular halides :



and in many coordination compounds, *e.g.* $Na[AlCl_4]$, $[AlCl_3(NH_3)]$, $[AlCl_3(PH_3)]$, etc., and as it belongs to a long period also a covalency of 6 in many compounds, *e.g.* $Na_3[AlF_6]$, $[Al(NH_3)_6]Cl_3$, etc., when the valency arrangement is octahedral, as is shown by the optical activity of the complex oxalate (Wahl and Andersin, 1927) :



and similar compounds. The rare earth metals also show a maximum covalency of 6.

The crystalline forms differ considerably : boron is tetragonal (?), the rare earth metals form either hexagonal or face-centred cubic (europium body-centred), aluminium face-centred cubic, gallium and indium tetragonal, and thallium both hexagonal and body-centred cubic lattices. The melting points also differ considerably.

The only non-metal in the group is boron. The rare earths (except scandium oxide) are strongly basic oxides ; boron trioxide B_2O_3 is weakly acidic and aluminium oxide weakly basic, but both are amphoteric, as are the oxides of the other elements of the *b* sub-group, except thallium. Boron forms several volatile hydrides, gallium forms a volatile Ga_2H_6 and solid hydrides of rare earth elements are described.

The small atomic volumes and the large charges on $B^{\cdots}$ and $Al^{\cdots}$ lead to the formation of covalent compounds and the trihalides of the *b* sub-group except thallium are volatile : aluminium chloride in the vapour (except at higher temperatures) exists as Al_2Cl_6. $GaCl_3$ is also largely associated to Ga_2Cl_6 in the vapour at 498°. The trihalides are hydrolysed by water. The rare earth chlorides MCl_3, however, are salt-like, not readily volatile and not hydrolysed. All the elements (even boron) form oxy-salts such as sulphates, but carbonates are formed only by rare earths, indium, and univalent thallium.

Corresponding salts of metals of the two sub-groups (except the ethyl-sulphates and acetylacetonates of scandium and indium) are not isomorphous and usually crystallise with different numbers of molecules of water. The

sulphates of metals of the *b* sub-group (except thallic sulphate) form alums $Me^{I}Me^{III}(SO_4)_2,12H_2O$, those of the *a* sub-group form double sulphates $Me^{I}Me^{III}(SO_4)_2,8H_2O$ of a different type.

Boron oxidises in air only on heating; aluminium is quite stable in air because of a thin protective oxide film; the rare earth metals and indium are stable in air, gallium oxidises only slightly but thallium readily in moist air. The rare earth metals oxidise on heating in air.

Organo-metallic compounds are formed by all the elements of the *b* sub-group, but not by the rare earths. Except aluminium, all the elements of the *b* sub-group are diamagnetic, whilst the rare earth metals are paramagnetic and gadolinium is ferromagnetic.

Boron

Borax $Na_2B_4O_7,10H_2O$, called *tincal*, was obtained in the Middle Ages from Tibet and used as a flux. Some Roman *terra sigillata* have a borate glaze, probably made with boric acid from Tuscany. Homberg (1702) obtained a crystalline *sal sedativum* by distilling green vitriol ($FeSO_4.7H_2O$) with borax. This was *boric acid* (H_3BO_3), which Geoffroy in 1732 obtained from borax and sulphuric acid. Baron in 1747 obtained borax from it by the action of sodium carbonate. Boric acid on heating forms boron trioxide B_2O_3, and Lavoisier suggested that this was the oxide of an unknown radical, first isolated as an olive-brown powder by Davy in 1807 by electrolysing moist boric acid and called by him *boron* in 1812. In 1808 Gay-Lussac and Thenard, and Davy, obtained boron by heating B_2O_3 with potassium and described its properties.

Boron is formed on heating boron trioxide or potassium fluoborate with potassium or sodium:

$$B_2O_3 + 6K = 2B + 3K_2O, \quad \text{or} \quad KBF_4 + 3K = B + 4KF,$$

or with magnesium powder:

$$B_2O_3 + 3Mg = 2B + 3MgO, \quad \text{or} \quad 2KBF_4 + 3Mg = 2B + 2KF + 3MgF_2.$$

The amorphous brown powder left after boiling the reaction product with dilute hydrochloric acid contains at most 86 p.c. of boron, but it can be purified by treatment with hydrofluoric acid and fusion with B_2O_3 in a stream of hydrogen (Moissan, 1892).

EXPT. 1.—Heat 2 g. of a mixture of 5 g. of magnesium powder and 15 g. of fused and powdered B_2O_3 in a covered crucible until a violent reaction occurs. After cooling, place the crucible in hydrochloric acid (1 : 2) in a beaker. Heat, filter, and wash the boron with hot water. Dry in a steam oven. The boron tends to form a brown colloidal solution on washing.

Moissan's amorphous boron is a brown powder, s.g. 2·45, which is unaltered in air at room temperature but smoulders at 700° with formation of B_2O_3 and some BN on the surface. It burns brilliantly when heated in oxygen or dropped on fused potassium chlorate, combines with nitrogen at 1200°, and reduces silica on heating: $4B + 3SiO_2 = 3Si + 2B_2O_3$.

Moissan's boron always contains oxygen, and is perhaps a solid solution of a suboxide B_4O_3 or B_3O in boron. Pure boron is insoluble in 40 p.c. nitric acid, which dissolves a large part of Moissan's boron, leaving a residue of purer boron (Weintraub, *Ind. Eng. Chem.*, 1911, **3**, 299; 1913, **5**, 106; *J.S.C.I.*, 1910, **29**, 23; Ray, *J.C.S.*, 1914, **105**, 2162).

Amorphous boron (92 p.c.) deposits on the cathode in the electrolysis of fused borax or a fused mixture of $2B_2O_3 + MgO + MgF_2$ at 1100°; it is washed with hydrochloric acid (Audrieth, 1927).

Pure boron is formed by striking an alternating current arc between water-cooled copper electrodes in an atmosphere of hydrogen and boron trichloride vapour in a glass globe (Pring and Fielding, *J.C.S.*, 1909, **95**, 1497). The brown powder collecting on the electrodes fuses to globules which drop off. It is a black, very hard amorphous solid with a conchoidal fracture, s.g. 2·34, m.p. 2300°, volatilising appreciably at 1600°. It is not oxidised on strongly heating in air and only slowly by concentrated nitric acid. By using a condensed high-frequency oscillatory discharge between tungsten or molybdenum electrodes in an atmosphere of boron trichloride and hydrogen, Hackspill (1931) obtained bright very hard plates of boron, with a metallic lustre, s.g. 2·33. Plates and needles are deposited on a tantalum wire heated above 1300° in a mixture of BBr_3 vapour and hydrogen. The X-rays indicate a crystalline (probably tetragonal) lattice (Laubengayer, etc., *J.A.C.S.*, 1943, **65**, 1924).

What were once regarded as crystalline forms of boron are all impure. By fusing amorphous boron with aluminium in a graphite crucible and dissolving the aluminium with hydrochloric acid, three kinds of crystals are obtained:

(i) black *adamantine boron* (Deville and Wöhler, 1856), crystals (probably monoclinic) of AlB_{12} (Hampe, 1876);

(ii) yellow or brown crystals of $Al_3C_2B_{48}$ (Hampe) or $Al_3C_2B_{44}$ (Biltz, 1910);

(iii) scales of *graphitoidal boron*, AlB_2 (Wöhler, 1867; Funk, 1925).

The metallic **borides**, usually formed (from all metals except Cu, Ag and Au) at high temperatures in the electric furnace, are of varying types. Those of alkaline earth metals $M^{II}B_6$ have a diamond lattice of boron atoms linked by covalencies, and metal atoms in the gaps: each boron is surrounded by 4 metal atoms and each metal has 24 neighbouring boron atoms. These, and the borides of Al, Mo and W, are very hard, but the hardest (and probably the hardest substance known) is carbon boride (Clark and Howard, *J.A.C.S.*, 1943, **65**, 2115), CB_4 (formerly regarded as CB_6). Beryllium and magnesium (Mg_3B_2) borides differ from most other metal borides in being attacked by acids, evolving hydrides of boron.

Boron Hydrides

Equal weights of dry powdered B_2O_3 and magnesium powder heated in a crucible react with incandescence and form **magnesium boride** Mg_3B_2:

$$B_2O_3 + 6Mg = Mg_3B_2 + 3MgO.$$

This reacts with dilute hydrochloric or sulphuric acid evolving hydrogen containing *boron hydrides* or *boranes*.

The gas has a peculiar smell and burns with a green-edged flame (F. Jones, *J.C.S.*, 1879, **35**, 41 ; 1881, **39**, 213). Ramsay and Hatfield (1901) thought it contained B_3H_3 but this was probably a mixture. Beryllium boride gives a gas less contaminated with silicon hydride (from silicon in the magnesium). The several boron hydrides have been investigated by Stock and co-workers (*The Hydrides of Boron and Silicon*, 1933), and by Schlesinger and co-workers (*J.A.C.S.*, 1931 f.). It is noteworthy that the expected hydride BH_3 is not known.

Magnesium boride powder is slowly dropped into 10 p.c. hydrochloric acid at 50° or 8*N* H_3PO_4 at 70° by the arrangement shown in Fig. 190. The gas is

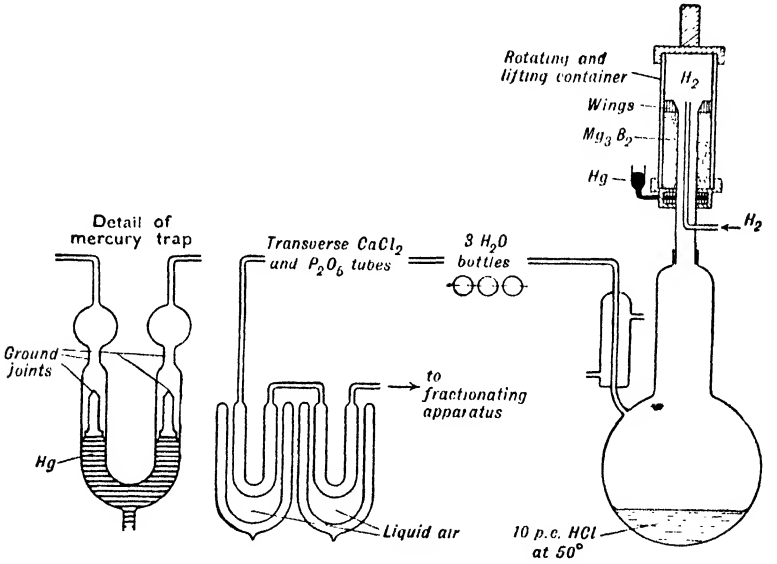


FIG. 190.—Preparation of boron hydrides.

carried off by a current of hydrogen, dried, and the boranes liquefied by cooling in liquid air or liquid nitrogen. Absence of air and grease is essential in the subsequent treatment, and the mercury trap shown is used instead of greased stopcocks. Diborane B_2H_6 is decomposed by water and is not present in the gas. The liquid condensed contains B_4H_{10} (the main product), B_5H_9 and B_6H_{10}. The properties and sources of the boron hydrides are summarised below :

	B_2H_6	B_4H_{10}	B_5H_9	B_5H_{11}	B_6H_{10}	$B_{10}H_{14}$
m.p. -	−165·5°	−120°	−46·6°	−129°	−65·1°	+99·7°
b.p. -	−92·5°	+18°	0°/66 mm.	0°/57 mm.	0°/7 mm.	213°
	(gas)	←		(liquids)		→ (solid)
Stability -	+	−	++	−−	−	+
Source -	B_4H_{10}	crude gas	B_4H_{10}	B_2H_6	crude gas	B_2H_6

B_2H_6 is formed by heating B_4H_{10} at 100°, when hydrogen, $B_{10}H_{14}$ and traces of B_5H_9 and B_6H_{10} are also formed, and condensing from the gas in liquid air. A more convenient preparation is by the action of an electric discharge on a mixture of hydrogen and BCl_3 or better BBr_3 vapour at low pressure, when B_2H_5Cl (or B_2H_5Br) is formed as an intermediate product: $2BCl_3 + 5H_2 = B_2H_5Cl + 5HCl$, and decomposes: $6B_2H_5Cl = 5B_2H_6 + 2BCl_3$ (Schlesinger and Burg, 1931). With BBr_3 the HBr (less volatile) can be separated by fractionation. B_2H_6 is very stable in absence of grease, air and moisture, but slowly decomposes at room temperature, forming B_5H_{11} and some $B_{10}H_{14}$, and is rapidly decomposed by water: $B_2H_6 + 6H_2O = 2H_3BO_3 + 6H_2$.

B_4H_{10} is stable and is formed by the action of sodium on B_2H_5I:

$$2B_2H_5I + 2Na = B_4H_{10} + 2NaI;$$

it is only slowly hydrolysed by water: $B_4H_{10} + 12H_2O = 4H_3BO_3 + 11H_2$.

B_5H_9 is very stable and is formed by heating B_2H_6 with dry HCl at 125°; or by heating a current of B_4H_{10} vapour at 200°, hydrogen (and perhaps B_5H_{10}) being also formed. It has a very nauseous smell, does not react with HCl and only very slowly with water: $B_5H_9 + 15H_2O = 5H_3BO_3 + 12H_2$, and dissolves almost unchanged in alkali solution.

B_5H_{11} is very unstable and is formed, with some $B_{10}H_{14}$, on keeping B_2H_6 for some months at room temperature, but itself also decomposes:

$$2B_5H_{11} = B_{10}H_{14} + 4H_2.$$

B_6H_{10}, separated from the crude gas, decomposes on standing to H_2 and a yellow solid, and is slowly hydrolysed by water. On acidifying its solution in alkali, hydrogen is evolved.

$B_{10}H_{14}$, formed by heating B_2H_6 or B_4H_{10}, is solid, stable below 170° but decomposing at higher temperature. It is insoluble in water but is slowly decomposed: $B_{10}H_{14} + 30H_2O = 10H_3BO_3 + 22H_2$; it is soluble in alkali and on acidification hydrogen is evolved; it does not react with HCl.

Halogen substitution products of B_2H_6 and B_4H_{10} are formed by the action of dry HCl, HBr or HI gas in presence of aluminium chloride:

$$B_2H_6 + HCl = B_2H_5Cl + H_2.$$

The action of halogens is violent, but by cooling and under reduced pressure substitution products are formed: iodine gives only BI_3.

B_2H_6 and B_4H_{10} react with solid alkalis or solutions of alkalis to form unstable **hypoborates**:

$$B_4H_{10} + 4KOH = 4KOBH_3 + H_2.$$

These are strong reducing agents and evolve hydrogen when acidified:

$$2KOBH_3 + 2HCl + 2H_2O = 2HBO_2 + 2KCl + 5H_2.$$

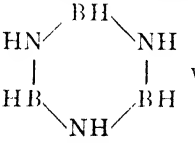
On heating solid potassium hypoborate, metallic potassium distils:

$$10KOBH_3 = 2K_3B_5O_3 + 4K + 11H_2 + 4H_2O.$$

The formula may be $K_2[B_2H_4(OH)_2]$.

The boranes show some acidic character in reacting with alkali metals and with anhydrous ammonia. B_2H_6 reacts with sodium amalgam to form $[B_2H_6]Na_2$ and B_4H_{10} reacts with sodium to form $[B_4H_{10}]Na_4$. With ammonia the compounds $B_2H_6,2NH_3$, $B_4H_{10},4NH_3$ and $B_{10}H_{14},6NH_3$ are formed; B_5H_{11} reacts as follows: $B_5H_{11}+4NH_3=B_5H_9,4NH_3+H_2$. $B_2H_6,2NH_3$ is an electrolyte in liquid ammonia and has been formulated as an ammonium salt $[B_2H_4](NH_4)_2$.

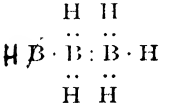
On heating $B_2H_6,2NH_3$ or $B_4H_{10},4NH_3$, hydrogen is evolved and **triborine triamine** is formed: the molecule is a flat hexagonal ring:



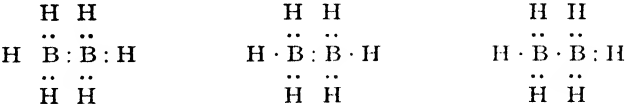
with a large resonance energy (Bauer, *J.A.C.S.*, 1938, **60**, 524). By the action of dry HCl the three BH groups form BCl.

By the action of excess of CO on B_2H_6 under pressure **borine carbonyl** BH_3CO is formed: $B_2H_6+2CO \rightleftharpoons 2BH_3CO$, which reacts with ammonia to form the stable $BH_3CO(NH_3)_2$.

The **structure of the boranes** is a difficult problem, as they show anomalous valencies. In B_2H_6 the two boron atoms have 6 electrons and with 6 from the six hydrogens there are only 12 to form seven bonds, leaving two electrons short. It has been suggested that two or more single electron bonds are formed, *e.g.*



but these would confer paramagnetism, which is not found. This has been got over by assuming resonance (Pauling, *J.A.C.S.*, 1936, **58**, 2403). Bauer (*ibid.*, 1937, **59**, 1096; 1938, **60**, 805) finds from electron diffraction that the bonds B—H and B—B are longer than ordinary single covalencies, which indicates some single electron bond or no-electron bond character, so that there may be resonance among arrangements such as:



Wiberg (*Ber.*, 1936, **69**, 2816) stresses the feebly acidic properties of the boranes and regards them as unsaturated polybasic acids, *e.g.* $[B_2H_4]H_2$ or $\overset{+}{H}H_2\overset{-}{B}=\overset{-}{B}H_2\overset{+}{H}$ similar to ethylene, etc. In his formulae each boron is surrounded by 8 electrons. The acidic character arises because the B_2H_4 radical, although not electrovalent, can accept protons, and the two protons are inside the electron shell of the B_2H_4 (see Welch, *J.S.C.I.*, 1939, **58**, 869; Schlesinger and Burg, *Chem. Reviews*, 1942, **31**, 1; Bauer, *ibid.*, 43).

Boron Halides

Halogen compounds of boron are all covalent and are decomposed by water: they have the formula BX_3, but a dichloride B_2Cl_4 or $Cl_2B{\cdot}BCl_2$ is known.

BF_3 colourless gas, condensing to colourless mobile liquid, m.p. $-127°$, b.p. $-101°$.
B_2Cl_4 colourless liquid, b.p. $0°/40$ mm.
BCl_3 colourless mobile liquid, m.p. $-107°$, b.p. $12{\cdot}5°$, s.g. $1{\cdot}434$ at $0°$, $1{\cdot}349$ at $11°$.
BBr_3 colourless viscous liquid, s.g. $2{\cdot}650$ at $0°$, m.p. $-46°$, b.p. $90{\cdot}1°/740$ mm.
BI_3 white leafy crystals, m.p. $43°$, s.g. $3{\cdot}35$ at $50°$, b.p. $210°$.

Boron trifluoride BF_3 is obtained by the spontaneous combustion of boron in fluorine, or by heating a mixture of fluorspar (or potassium fluoborate KBF_4, or cryolite Na_3AlF_6), boron trioxide and concentrated sulphuric acid:

$$B_2O_3 + 3CaF_2 + 3H_2SO_4 = 2BF_3 + 3CaSO_4 + 3H_2O.$$

It is most conveniently made by heating a mixture of 4 g. of KBF_4 with 3 g. of powdered B_2O_3 at 518° (Hellriegel, 1937), and is also formed on heating diazobenzene fluoborate (Biltz, 1932). The gas is collected over mercury.

When a borate is mixed with powdered fluorspar and concentrated sulphuric acid and a little of the paste held on platinum wire in a Bunsen flame a green flame is produced (test for borate).

Boron fluoride fumes strongly in moist air, and when passed into water it forms a precipitate of boric acid which redissolves if more BF_3 is passed in, giving a solution of **fluoboric acid** HBF_4:

$$4BF_3 + 3H_2O = B(OH)_3 + 3HBF_4$$
$$B(OH)_3 + 4HF = HBF_4 + 3H_2O.$$

This is more easily made by dissolving boric acid in cooled 50 p.c. hydrofluoric acid and evaporating. On distillation a liquid of the composition $BF_3{,}2H_2O$ is formed, and when saturated with BF_3 the composition is $BF_3{,}H_2O$: it is doubtful if these are compounds. The acid forms **fluoborates** (or *borofluorides*), *e.g.* KBF_4, an amphorous white solid precipitated by a potassium salt. The tendency of boron to show a covalency of 4 is here apparent. Fluoborates are formed in solution from boric acid and acid fluorides:

$$H_3BO_3 + 2NaHF_2 = NaBF_4 + NaOH + 2H_2O.$$

They are decomposed by heat: $KBF_4 = KF + BF_3$. The acids $HClO_4$ and HBF_4 show similarities, especially in forming salts with organic bases. The similarity in the reactions of BF_3 and SiF_4 with water should be noted.

Boron trichloride BCl_3 is formed by burning amorphous boron in dry chlorine (Davy, 1810; Briscoe and Robinson, *J.C.S.*, 1925, **127**, 696), and by passing dry chlorine over a strongly heated mixture of boron trioxide and charcoal (Dumas, 1826): $B_2O_3 + 3C + 3Cl_2 = 2BCl_3 + 3CO$. It is condensed in a glass

worm-tube in a freezing mixture and is freed from chlorine by distillation over mercury. It is a gas at room temperature.

Boron chloride is formed by heating B_2O_3 with PCl_5 in a sealed tube at 150°: $B_2O_3 + 3PCl_5 = 2BCl_3 + 3POCl_3$, or heating amphorous boron with CCl_4 in a sealed tube at 250°: $4B + 3CCl_4 = 4BCl_3 + 3C$.

Boron trichloride fumes strongly in moist air and is irreversibly hydrolysed by water: $BCl_3 + 3H_2O = B(OH)_3 + 3HCl$.

Boron dichloride B_2Cl_4, b.p. 0°/40 mm., is obtained in small yield by striking an arc with a zinc anode under liquid BCl_3 (Stock, Brandt and Fischer, 1925). It slowly decomposes into BCl_3 and boron at room temperature, reacts with water to form B_2O_2 (p. 414) and with alkali solution it evolves hydrogen:

$$B_2Cl_4 + 6NaOH = 2NaBO_2 + 4NaCl + 2H_2O + H_2.$$

Boron tribromide BBr_3 is formed similarly to the chloride (Hoskyns-Abrahall, *J.C.S.*, 1892, **61**, 650). **Boron tri-iodide** BI_3 is formed by passing a mixture of boron trichloride vapour and hydrogen iodide through a heated tube (Moissan, 1891–2). It burns when heated in oxygen: $4BI_3 + 3O_2 = 2B_2O_3 + 6I_2$. It is soluble in benzene and carbon disulphide but reacts with ether:

$$BI_3 + 3(C_2H_5)_2O = B(OC_2H_5)_3 + 3C_2H_5I.$$

Boron Oxides and Oxyacids

The typical oxide is **boron trioxide** B_2O_3, formed as a hygroscopic glass on heating boric acid to redness: $2H_3BO_3 = B_2O_3 + 3H_2O$, and as a white powder on dehydrating boric acid over phosphorus pentoxide in vacuum and slowly heating to 200° (Tiede, etc., 1923; McCulloch, *J.A.C.S.*, 1937, **59**, 2650; Kelly, *ibid.*, 1941, **63**, 1137). The m.p. is 294° (Taylor and Cole, *J.A.C.S.*, 1934, **56**, 1648) and the s.g. 1·805, whilst the glass, s.g. 1·795 (Briscoe, etc., *J.C.S.*, 1926, 70), has no definite m.p. but softens gradually and becomes fluid at a red heat. It is notably volatile at 1000°. The solution of B_2O_3 rapidly hydrates to metaboric acid HBO_2, which more slowly forms orthoboric acid H_3BO_3 (Myers, *J.C.S.*, 1917, **111**, 172).

Common or **orthoboric acid** H_3BO_3 or $B(OH)_3$ (also called *boracic acid*) occurs in steam jets in Tuscany and is obtained by the action of hydrochloric or sulphuric acid on a concentrated solution of borax:

$$Na_2B_4O_7 + 2HCl + 5H_2O = 4H_3BO_3 + 2NaCl.$$

In the volcanic regions of Tuscany, jets of steam called *soffioni* escape from the ground; these contain steam, carbon dioxide, hydrogen sulphide, nitrogen, ammonia, and traces of boric acid, which is volatile in steam. The boric acid may have been produced by the action of superheated water on boron nitride: $BN + 3H_2O = H_3BO_3 + NH_3$, or on boron sulphide: $B_2S_3 + 6H_2O = 2H_3BO_3 + 3H_2S$, or on tourmaline, which contains 3–4 p.c. of B_2O_3 and is found *in situ*. In the modern process the steam is used to generate electric power and the boric acid crystallised from the condensed water (Conti, *J.S.C.I.*, 1925, **44**, 343T).

EXPT. 2.—To a hot concentrated solution of borax add concentrated hydrochloric acid till strongly acid to litmus. On cooling, scaly six-sided crystals of boric acid separate. Wash the crystals with cold water and recrystallise from hot water.

Boric acid is also made by passing sulphur dioxide into a suspension of the finely ground mineral colemanite in hot water, and crystallises on cooling :

$$Ca_2B_6O_{11} + 2SO_2 + 9H_2O = 2CaSO_3 + 6H_3BO_3.$$

Orthoboric acid forms soft pearly-white silky triclinic crystals (Fig. 191) with a greasy feel, sparingly soluble in cold but more readily in hot water (2·66 g. at 0°, 4·01 g. at 12°, 23·62 g. at 80°, in 100 g. H_2O). It is less soluble in solutions of acids.

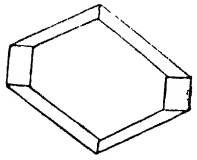


FIG. 191.—Crystal of boric acid.

Traces of boric acid occur in plants and animals (2·8 mg. H_3BO_3 per kg. of wheat flour, 1·1 mg. per lit. of milk) and a small amount seems necessary for healthy growth of plants, an excess being toxic.

Boric acid is very weak and ionises as a monobasic acid :

$$K_a' = [H^+]\,[H_2BO_3^-]/[H_3BO_3] = 6{\cdot}5 \times 10^{-10}$$

at 25° (Thiel and Siebenacker, 1934). A solution turns blue litmus a wine-red colour but has no action on methyl orange. It may be titrated as a monobasic acid with phenolphthalein if a large amount of glycerol is added, when a fairly strong complex monobasic acid is formed :

$$\begin{array}{l} \quad OH \\ B{-}OH \\ \quad OH \end{array} + \begin{array}{l} HO{\cdot}CH_2{\cdot}CHOH{\cdot}CH_2{\cdot}OH \\ \\ HO{\cdot}CH_2{\cdot}CHOH{\cdot}CH_2{\cdot}OH \end{array} = \begin{array}{l} \quad O' \\ B{-}O{\cdot}CH_2{\cdot}CHOH{\cdot}CH_2{\cdot}OH \\ \quad O{\cdot}CH_2{\cdot}CHOH{\cdot}CH_2{\cdot}OH \end{array} + H^+ + 2H_2O.$$

A piece of turmeric paper dipped in a solution of a borate acidified with hydrochloric acid becomes brownish-red on drying, and greenish-black if then moistened with alkali.

Boron trioxide shows feebly basic as well as acidic properties. Boric acid combines with sulphur trioxide, forming **boron hydrogen sulphate** $B(HSO_4)_3$, and when evaporated with phosphoric acid it forms **boron phosphate** BPO_4, insoluble in water and dilute acids but soluble in alkalis. In this respect boron resembles aluminium.

Orthoboric acid at 100° loses water : $H_3BO_3 = H_2O + HBO_2$, and forms **metaboric acid** HBO_2, O=B—OH or O←B—OH. **Polyboric acids** are said to be formed at higher temperatures (*e.g.* $H_2B_4O_7$ at 138°–140°, but Menzel, etc., *Z. anorg. Chem.*, 1934, **220**, 49, found only H_3BO_3 and HBO_2) with anions B_nO_{2n-1}, derived from H_3BO_3 according to the formula $nH_3BO_3 - (n+1)H_2O$, *e.g.* $H_2B_4O_7$, $H_3B_5O_9$, $H_4B_6O_{11}$ and $H_6B_8O_{15}$ (Kracek, Morey and Merwin, *Amer. J. Sci.*, 1938, **35A**, 143). Salts of some of these occur as minerals : ***borax*** $Na_2B_4O_7{,}10H_2O$, and ***kernite*** or ***rasorite*** $Na_2B_4O_7{,}4H_2O$, especially in

California; *colemanite* $Ca_2B_6O_{11},5H_2O$ in California and Asia Minor and formerly an important source of borates; the less common *ulexite* or *boronatrocalcite* $NaCaB_5O_9,8H_2O$ in Chile, and the Stassfurt mineral *boracite* $MgCl_2,2Mg_3B_8O_{15}$.

The Raman spectrum shows that the metaborate ion O=B—O′ or O←B—O′ is linear (Nielsen and Ward, *J. Chem. Phys.*, 1937, **5**, 201). The X-ray spectrum (Zachariasen, 1934) shows that orthoboric acid contains $B(OH)_3$ molecules in sheets 3·18 A. apart in a layer lattice, held together by hydroxyl bonds, and that metaborates are salts of a polymer $(HBO_2)_n$ in which each boron atom (as in H_3BO_3) is surrounded by three oxygen atoms in a plane and nearly equilateral triangle (Zachariasen, *J.A.C.S.*, 1931, **53**, 2123).

Orthoborates are infrequent: magnesium borate $Mg_3(BO_3)_2$ and the **esters**, *e.g.* $B(OC_2H_5)_3$, being best known.

Ethyl borate $B(OC_2H_5)_3$, discovered by Ebelmen in 1846, is formed when a borate is distilled with alcohol and concentrated sulphuric acid:

$$B(OH)_3 + 3C_2H_5OH \rightleftharpoons B(OC_2H_5)_3 + 3H_2O.$$

The vapour burns with a green flame (noticed by Geoffroy in 1702), used as a *test for a borate.*

EXPT. 3.—Add a little borax and concentrated sulphuric acid to methylated spirit in a flask fitted with a glass jet and wider glass tube, which acts as a Bunsen burner and removes the luminosity of the flame due to ether also formed. Heat the flask and kindle the vapour. A large green flame is formed (Fig. 192).

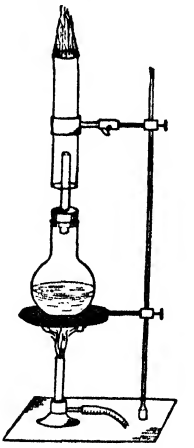


FIG. 192. Green flame of ethyl borate.

Most metallic borates are **metaborates**, which are precipitated from solutions of salts by borax solution:

$$BaCl_2 + Na_2B_4O_7 + 3H_2O = Ba(BO_2)_2 + 2H_3BO_3 + 2NaCl,$$

or formed in the dry way in *borax bead reactions* (Burgess and Holt, *Proc. C.S.*, 1903, **19**, 221):

$$CuO + Na_2B_4O_7 = Cu(BO_2)_2 + 2NaBO_2.$$

Sodium metaborate $NaBO_2,4H_2O$ crystallises in needles from a solution of borax in sodium hydroxide solution:

$$Na_2B_4O_7 + 2NaOH = 4NaBO_2 + H_2O.$$

Lead borate $Pb(BO_2)_2,H_2O$ is used as a paint drier.

The most important borate is *borax*, sodium tetraborate $Na_2B_4O_7,10H_2O$, which is extracted from Searle's Lake, California (2·86 p.c. borax), or made by crystallising kernite $Na_2B_4O_7,4H_2O$. It was formerly made by boiling colemanite with sodium carbonate solution:

$$Ca_2B_6O_{11} + 2Na_2CO_3 = Na_2B_4O_7 + 2NaBO_2 + 2CaCO_3,$$

crystallising borax from the filtrate, and converting the metaborate in the mother-liquor into borax by passing in carbon dioxide:

$$4NaBO_2 + CO_2 = Na_2B_4O_7 + Na_2CO_3.$$

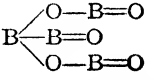
Common borax $Na_2B_4O_7,10H_2O$ is monoclinic and deposits below 62°; above this rhombohedral $Na_2B_4O_7,5H_2O$ ("octahedral" borax) crystallises. On heating it loses water, swelling considerably and giving anhydrous borax, which exists in three forms melting at 738°, 710° and 663° (Menzel, 1935) to a transparent glass. The solubility of borax is 3 g. at 10° and 99 g. at 100° in 100 g. water. The solution is hydrolysed and reacts alkaline:

$$Na_2B_4O_7 + 3H_2O \rightleftharpoons 2NaBO_2 + 2H_3BO_3 \text{ (conc. sol.)},$$
$$NaBO_2 + 2H_2O \rightleftharpoons NaOH + H_3BO_3 \text{ (dil. sol.)}.$$

Borax is used in the laundry to give a gloss on ironing, in making glazes and glasses, as a flux in soldering, and as an antiseptic, *e.g.* for washing oranges before packing. In the laboratory it is used in "borax bead" tests (see above).

Perborates.—Sodium perborate (Matthews, *Ind. Eng. Chem.*, 1911, **3**, 191) is obtained by the action of hydrogen peroxide and sodium hydroxide, or sodium peroxide, on cooled borax solution, or by the electrolysis of a solution of borax and sodium carbonate with a platinum gauze anode. It was considered to be a true perborate $NaBO_3,4H_2O$, but is probably a borate with hydrogen peroxide of crystallisation, $NaBO_2,3H_2O,H_2O_2$. It does not liberate iodine from concentrated potassium iodide solution. The dry compound ("perborax") is stable and is only sparingly soluble. The solution has bleaching and antiseptic properties and is stable at room temperature but evolves oxygen on warming. The solid loses $3H_2O$ at 50°–55°, and in vacuum at 120° it loses another molecule of water, leaving a yellow solid formulated as $(NaBO_2)_2O_2$, which with water evolves oxygen but does not liberate iodine from concentrated potassium iodide solution.

Lower oxides of boron.—The oxides B_2O_2 and B_4O_5, and salts corresponding with B_2O, have been described. These may all contain tervalent boron:



Ray (*J.C.S.*, 1922, 1088) by the action of dilute potassium hydroxide on magnesium boride obtained a crystalline salt $H_4B_2(OK)_2$ which evolves hydrogen with dilute acid and reduces iodine:

$$H_4B_2(OK)_2 + 2H_2SO_4 = 2KHSO_4 + B_2(OH)_2 + 2H_2,$$
$$B_2(OH)_2 + I_2 = B_2O_2 + 2HI.$$

$B_2(OH)_2$ corresponds with an oxide B_2O, from which B_2O_2 is formed by oxidation. Wiberg and Ruschmann (*Ber.*, 1937, **70**, 1393) formulate B_2O_2 as O=B—B=O, corresponding with an acid $H_4B_2O_4$, which they prepared in white crystals, evolving hydrogen in solution, by the reactions:

$$BCl_3 + 2B(OCH_3)_3 = 3B(OCH_3)_2Cl,$$
$$2B(OCH_3)_2Cl + 2Na = (CH_3O)_2B{\cdot}B(OCH_3)_2 + 2NaCl,$$
$$(CH_3O)_2B{\cdot}B(OCH_3)_2 + 4H_2O = (HO)_2B{\cdot}B(OH)_2 + 4CH_3OH.$$

Ray and Sinha (*J.C.S.*, 1941, 742) obtained colourless crystalline $(NH_4)_2B_2(OH)_2$ and $(NH_4)_2B_4O_6$ by the action of ammonia on the residue from the prolonged action of water on magnesium boride. On heating in vacuum these form the oxides B_2O_2 and B_4O_5, respectively.

Boron Compounds

Boron nitride BN was discovered by Balmain (1842–3), who determined its formula and noticed its green luminescence in a flame ; it is also phosphorescent (Tiede, etc., 1920). Boron nitride has the same lattice as graphite. It is a white infusible solid, formed from its elements at 1200°, but more easily by heating borax with ammonium chloride, washing with hydrochloric acid and then water, and drying (Wöhler, 1850) :

$$Na_2B_4O_7 + 2NH_4Cl = 2NaCl + H_2O + 2B_2O_3 + 2NH_3$$
$$B_2O_3 + 2NH_3 = 2BN + 3H_2O.$$

Pure boron nitride is best made by the action of ammonia gas on boron trichloride, when the **boron amide** first formed :

$$BCl_3 + 6NH_3 = B(NH_2)_3 + 3NH_4Cl$$

decomposes on heating, first into **boron imide** :

$$2B(NH_2)_3 = B_2(NH)_3 + 3NH_3,$$

and then into boron nitride (Stock, etc., 1901–8) :

$$B_2(NH)_3 = 2BN + NH_3.$$

Boron nitride is unchanged by mineral acids or alkali solutions, or chlorine at a red heat, but is decomposed on heating in steam or on fusion with alkali :

$$2BN + 3H_2O = B_2O_3 + 2NH_3,$$

or (slowly) by hydrofluoric acid : $BN + 4HF = NH_4BF_4$. When fused with potassium carbonate it forms potassium cyanate :

$$BN + K_2CO_3 = KBO_2 + KCNO.$$

Boron sulphide B_2S_3 is a white solid formed by direct combination of the elements at a very high temperature, or by heating B_2O_3 and carbon in carbon disulphide vapour :

$$2B_2O_3 + 3C + 3CS_2 = 2B_2S_3 + 6CO.$$

It sublimes in needle-shaped crystals on heating and is violently hydrolysed by water :

$$B_2S_3 + 6H_2O = 2H_3BO_3 + 3H_2S.$$

It is soluble in liquid ammonia to form an intensely yellow compound $B_2S_3,6NH_3$.

Boron pentasulphide B_2S_5 was said by Moissan (1892) to be formed from BI_3 and a solution of sulphur in carbon disulphide ; it is decomposed by water into boric acid, hydrogen sulphide and sulphur.

Hydrogen sulphide and boron tribromide form **metathioboric acid**, which can be obtained in white needles from a solution in benzene, in which it has a molecular weight corresponding with $H_3B_3S_4$. It is decomposed by water into boric acid and hydrogen sulphide and by heating at 300° it forms B_3S_3 (Stock and Poppenberg, 1901).

Boron hydrogen sulphate $B(HSO_4)_3$ is a white crystalline solid obtained from boric acid and sulphur trioxide : $H_3BO_3 + 3SO_3 = B(HSO_4)_3$.

Boron cyanate (Forbes and Anderson, *J.A.C.S.*, 1940, **62**, 761) is formed by the reaction $BBr_3 + 3AgCNO = B(CNO)_3 + 3AgBr$ in dry benzene, and **boron thiocyanate** $B(CNS)_3$ by the action of lead or silver thiocyanate on boron bromide (Miquel, 1877; Cocksedge, *J.C.S.*, 1908, **93**, 2177). Both are white crystalline solids.

Aluminium

Aluminium occurs to the extent of 7·3 p.c. in the earth's crust (next in abundance to oxygen and silicon) in many silicate rocks (felspar, augite, hornblende, tourmaline, micas), and in the secondary formations clay ($Al_2O_3,2SiO_2,2H_2O$) and slate (clay hardened and laminated by pressure). The oxide Al_2O_3 occurs as *corundum* and impure as *emery*, and hydrated as *diaspore* Al_2O_3,H_2O, *gibbsite* $Al_2O_3,3H_2O$, *laterite* (mostly gibbsite) and *bauxite* (mostly colloidal Al_2O_3,H_2O with diaspore and gibbsite in varying amounts). *Cryolite* Na_3AlF_6 (Greek *kryos*, frost) is a semi-transparent rock found in Greenland. *Orthoclase* (or potash) *felspar* $KAlSi_3O_8$ (or $K_2O,Al_2O_3,6SiO_2$) is a constituent of primary rocks such as granite, and by the combined action of water and atmospheric carbon dioxide it " weathers " into soluble potassium salts and insoluble clay :

$$2KAlSi_3O_8 + 2H_2O + CO_2 = K_2CO_3 + Al_2O_3,2SiO_2,2H_2O + 4SiO_2.$$

The quartz crystals and mica scales of the granite remain in the fine deposit of china clay or kaolin. Common clay is contaminated with limestone, quartz and oxides of iron and titanium. Aluminium compounds are not absorbed (except in traces) from the soil by plants, except mosses.

Alum was known to the Egyptians (*ybn*), Greeks (στυπτηρία) and Romans (*alumen*) and used as a mordant. Paracelsus said it was not a vitriol (with a metallic basis) and Pott (1746) showed that it is derived from a peculiar earth *alumina*, which Marggraf (1754) isolated from clay. Davy (1807–10) isolated the impure metal, which he called aluminum (the modern American name). A purer metal was obtained by Oersted (1825) by heating the amalgam formed by the action of excess of anhydrous aluminium chloride on potassium amalgam, and by Wöhler (1827) by heating anhydrous aluminium chloride with potassium. Bunsen (1854) and independently Deville (1854) obtained the metal by the electrolysis of fused sodium aluminium chloride $NaAlCl_4$ (fused $AlCl_3$ is almost non-conducting), or by heating it with sodium :

$$NaAlCl_4 + 3Na = 4NaCl + Al.$$

The second method was developed technically but was expensive, the price of the metal over a long period being about 70*s.* per kg. Cheap aluminium was first made in 1889 by the electrolysis of a solution of aluminium oxide in fused cryolite (Na_3AlF_6), the process being patented almost simultaneously in 1886 by Héroult in France and by Hall in America, the two methods differing only in detail (*Ind. Eng. Chem.*, 1911, **3**, 143; 1929, **21**, 120). The price dropped between 1890 and 1900 from 25*s.* to 2*s.* per kg.; in 1932 it was 1*s.* 6*d.* On account of the small chemical equivalent (9) of aluminium and its very high heat of oxidation : $2Al + \frac{3}{2}O_2 = Al_2O_3 + 380$ k. cal., a large expenditure of

energy is required, which can be obtained economically only from cheap water power.

Although attempts have been made to produce aluminium from clay, the actual source is the impure hydrated oxide *bauxite* (largely obtained in France, the U.S.A., Guiana and Hungary) or *laterite*. As this contains silica and ferric and titanium oxides it is first treated to obtain pure alumina.

(i) In the old process the bauxite is heated to bright redness with sodium carbonate to form sodium aluminate $NaAlO_2$, alumina being feebly acidic. The mass is rapidly lixiviated, forming finely divided oxide of iron (*red mud*) which can be used for purifying coal gas, and a solution of sodium aluminate, from which a granular precipitate of aluminium hydroxide is thrown down by carbon dioxide at 50°–60°: $2NaAlO_2 + CO_2 + 3H_2O = Na_2CO_3 + 2Al(OH)_3$. On igniting the precipitate Al_2O_3 is obtained, and the solution of Na_2CO_3 is evaporated and used again.

(ii) In the **Bayer process** (Lowe, *Chem. Trade J.*, 1923, **73**, 361) the calcined bauxite is digested with caustic soda solution under 80 lb. pressure, giving a solution of sodium aluminate and a residue of oxide of iron which cannot be used for any purpose. The aluminate solution is stirred at 25°–35° with precipitated alumina, when about 70 p.c. of the alumina in solution is deposited as a sandy precipitate of hydroxide $Al(OH)_3$, which is easily washed and on ignition at 1200° yields pure alumina.

The purified alumina is then dissolved in fused cryolite and electrolysed between carbon electrodes.

The electric furnace (Fig. 193) consists of an iron box, 6 ft. by 3 ft. by 3 ft., lined with blocks of carbon which form the cathode. The anodes are carbon rods set in a row about 2–3 in. above the bottom of the trough. The electrolyte is a solution of alumina (m.p. 2050°) in fused cryolite (now mostly artificial, p. 423), sometimes with fluorspar or AlF_3, the temperature being 875°–950° (Anderson, *The Metallurgy of Aluminium and Aluminium Alloys*, New York, 1925; Edwards, Frary and Jeffries, *The Aluminium Industry*, New York, 1930).

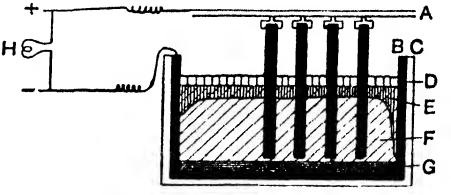


FIG. 193.—Electric furnace for aluminium: A. carbon anodes; B. carbon lining; C. cast-iron vessel; D. carbon powder protection; E. crust of solidified electrolyte; F. molten electrolyte; G. molten metal; H. low voltage charge control lamp.

The eutectic point for a mixture of Al_2O_3, cryolite and CaF_2 is 868°, and occurs when these are in the proportions 17·7 : 59·3 : 23. In practice, the mixture used may be Al_2O_3 5–10, cryolite 90–95, and if fluorspar is added, about 36 p.c. of the cryolite. An E.M.F. of 5–6 volts, and an anodic current density of 100 amp. per sq. dm., corresponding with a total current of 16,000–30,000 amp., are used. The energy consumption is 20–25 k.w.h. per kg. Al.

The alumina is electrolysed, the metal (m.p. 660°) forms a pool below the anodes, and the oxygen liberated burns the anodes to CO and CO_2 in about equal volumes.

Unless a large excess of alumina is present some cryolite decomposes and gaseous carbon tetrafluoride CF_4 is evolved from the carbon anodes (Newman and Brown, *Ind. Eng. Chem.*, 1930, **22**, 995). The charge is covered with a layer of carbon and fresh alumina is stirred in from time to time. The decomposition is indicated by a rise in resistance, the shunted lamp brightening. The technical metal is 99 p.c. Al, the chief impurities being iron and silicon.

Pure aluminium (99·98–99·99 p.c.) is made by **Hoopes' process** (1900). A liquid aluminium-copper anode is covered with fused cryolite and barium fluoride, on which floats a cathode of pure molten aluminium. The very pure metal differs in many properties from the 99 p.c. metal.

Aluminium is silver-white when pure (it has been distilled in high vacuum on to glass for telescope mirrors) but has a blue tinge when not quite pure. It is light (s.g. 2·70) and rather soft but with a high tensile strength, and finds many uses (Frary, *Ind. Eng. Chem.*, 1934, **26**, 1231).

Aluminium crystallises in a face-centred cubic lattice. Large single crystals can be obtained (Carpenter, *Nature*, 1930, **126**, 17). The metal can be cast; at 100°–150° it can be wrought, rolled, or drawn, but it becomes brittle at 600°. It is a good conductor of heat and electricity (for equal *weights* it is a better conductor than copper) and it is used for electric cables. The *powder* made by stamping pieces of thin sheet in oil really consists of thin flakes.

Aluminium can be soldered only with a special solder (Al 2·25 + phosphor-tin 0·75 + zinc 17 + tin 80), which is first applied to the metal by heating to 600°, and the two surfaces then pressed together. The most satisfactory joint, however, is an autogenous blowpipe or electric weld.

About one-thousandth of the weight of aluminium added to molten steel before casting removes oxygen and nitrogen, forming Al_2O_3 and AlN, and prevents blow-holes in castings. It reacts very violently with silicon steels.

Aluminium is unchanged in pure dry air, a transparent oxide film less than 0·00001 mm. thick being formed, but it corrodes in impure air (Vernon, *T. Faraday Soc.*, 1927, **23**, 113). Aluminium can be dyed on a 0·00004 mm. protective oxide film formed by anodic oxidation in 3 p.c. chromic acid; the process can also be used for some aluminium alloys. If the metal is rubbed with moist mercuric chloride the oxide film is broken and oxidation occurs, with evolution of heat and formation of moss-like excrescences of alumina. Amalgamated aluminium foil is a useful reducing agent in neutral solutions. Aluminium precipitates copper, lead and zinc from solutions of their salts. Aluminium powder burns brilliantly when heated in air.

Although only superficially attacked by pure water, aluminium is strongly attacked by sea water and some salt solutions, *e.g.* $MgCl_2$, which remove the oxide film. Dilute sulphuric acid has very little action and *pure* aluminium is almost unattacked by dilute or concentrated nitric acid or ammonium nitrate. Dilute or concentrated hydrochloric acid readily dissolves ordinary aluminium: $2Al + 6HCl = 2AlCl_3 + 3H_2$, but 99·99 p.c. aluminium is said to resist concentrated hydrochloric acid for many hours. Concentrated sulphuric acid attacks

aluminium only when heated: $2Al + 6H_2SO_4 = Al_2(SO_4)_3 + 3SO_2 + 6H_2O$, but phosphoric acid attacks it strongly: $2Al + 2H_3PO_4 = 2AlPO_4 + 3H_2$.

A cell with an aluminium electrode in alkali carbonate, phosphate, or borate, or soap, solution, acts as an alternating current rectifier, since it passes current only when the aluminium is the cathode.

Aluminium readily dissolves in alkali hydroxide solutions, forming aluminates: $2Al + 2NaOH + 2H_2O = 2NaAlO_2 + 3H_2$. It dissolves in a hot concentrated solution of sodium carbonate:

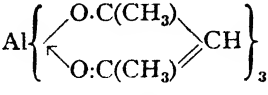
$$2Al + Na_2CO_3 + 3H_2O = 2NaAlO_2 + CO_2 + 3H_2,$$

and in hot concentrated ammonia it forms aluminium hydroxide and hydrogen (Smith, *J.S.C.I.*, 1904, **23**, 475).

The great evolution of heat in the oxidation of aluminium is applied in the *thermit process* (Goldschmidt, *J.S.C.I.*, 1898, **17**, 543, 584) for reducing metallic oxides (*e.g.* Cr_2O_3, MnO_2), and for the production of molten iron for welding broken articles *in situ*. A mixture of aluminium powder and oxide of iron (" smithy-scales ") in a crucible is ignited by a burning magnesium wire. A violent reaction occurs: $2Al + Fe_2O_3 = 2Fe + Al_2O_3$, and molten iron covered with a layer of molten alumina is formed. The iron is tapped from below directly on to the joint to be welded.

Aluminium alloys are used for many purposes requiring light strong metal and can be cast and wrought. Aluminium-silicon alloys (10–13 p.c. Si) are used for casting. *Duralumin*, which can be worked hot or cold, and is hardened by quenching from 350°–530° in water and heat-treating at 100°–200°, contains 4 p.c. of copper and about 0·5 p.c. each of magnesium and manganese. *Y-alloy* contains 4 p.c. of copper, 2 of nickel and 1 of magnesium, and can be both wrought and cast. *Aluminium bronze* may be 90 copper and 10 aluminium and generally contains some iron and a little tin. Some alloys have good electrical conductivity with considerable strength, and some contain several metals, *e.g.* *E-alloy* has 20 p.c. of zinc, 2·5 of copper, and 0·5 each of magnesium and manganese, and is made stronger by heat treatment (tensile strength 87,100 lb. per sq. in. as compared with 60,000 for steel) (Corson, *Aluminium and its Alloys*, 1926).

Aluminium is tervalent and forms the ion $Al^{\cdots}$ as well as covalent compounds, in which it tends to assume the coordination numbers (maximum covalencies) of 4, as in $NaAlCl_4$ and Al_2Cl_6 (p. 424), and 6, as in Na_3AlF_6 and the acetylacetone compound:



with an octahedral arrangement of bonds: the complex oxalate with this arrangement of bonds has been resolved into optically active forms (see p. 222).

Since alumina is a fairly weak base the aluminium salts are hydrolysed in solution and show an acid reaction.

Aluminium Oxide and Hydroxide

Aluminium oxide (*alumina*) Al_2O_3 occurs in rhombohedral crystals (always containing traces of the isomorphous gallium oxide Ga_2O_3) as *corundum*, nearly as hard as diamond. It is found in India, Burma, Ontario and North Carolina, but is mostly mined in the Transvaal *Emery* is an impure variety, consisting of a fine-grained aggregate of 50–60 p.c. of corundum and 30–40 p.c. of magnetite (Fe_3O_4), with other minerals, which occurs in Naxos, in Asia Minor, Australia and the U.S.A. : it is also very hard and is used in grinding and polishing.

Corundum when transparent forms a number of gems : *oriental topaz* (yellow), *sapphire* (blue, due to ferrous, chromium or titanium oxides), *ruby* (red, due to chromic oxide), *oriental amethyst* (violet, due to manganese), *oriental emerald* (green) (Stilwell, *J. Phys. Chem.*, 1926, **30**, 1441).

Artificial rubies are produced (Verneuil, 1902) by strewing powdered alumina containing 2·5 p.c. of Cr_2O_3 through the centre of an oxyhydrogen flame. The fused mass or " boule," caught on an alumina rod, forms a single crystal, which can be cut. *Artificial sapphires* are made by adding 1·5 p.c. of Fe_3O_4 and 0·5 p.c. of TiO_2 and a reducing flame is used.

Artificial corundum, known under trade names such as *alundum*, is used as a basic refractory and abrasive. It is made by fusing bauxite in an arc furnace at 3000°, allowing impurities to settle, cooling, and crushing the upper part. The powder may be mixed with a little clay and felspar, moulded, dried, and fired in a porcelain kiln at 1500°.

Bauxite cement (*ciment fondu*) is made by fusing nearly equal weights of bauxite and lime. The clinker is finely ground. This cement resists the action of sea water.

Two *crystalline varieties of alumina* are : α-Al_2O_3, hexagonal-rhombohedral corundum, s.g. 3·95–4·0, insoluble in acids, stable between 500° and 1500° ; γ-Al_2O_3, cubic, s.g. 3·42–3·64, hygroscopic, soluble in acids, formed by heating aluminium hydroxide below 950° (at higher temperatures it forms α-Al_2O_3).

Very pure alumina is made by calcining ammonia alum (p. 429). The m.p. of α-Al_2O_3 is 2050° and the b.p. 2980°. Strongly calcined alumina dissolves with difficulty in acids or alkalis.

Alkali hydroxide or ammonia gives with an aluminium salt solution a white gelatinous precipitate of **aluminium hydroxide**, which is readily soluble in excess of sodium or potassium hydroxide but almost insoluble in dilute ammonia. The precipitate is amorphous and dries to a glassy solid. When partly dehydrated at 200°–250° this adsorbs moisture, etc., very readily. This *alumina gel* is used as an adsorbent and drying agent (Johnson, *J.A.C.S.*, 1912, **34**, 911 ; Dover and Marden, *ibid.*, 1917, **39**, 1609 ; Munro and Johnson, *Ind. Eng. Chem.*, 1925, **17**, 88).

An interesting application of alumina gel is in *chromatographic analysis*, depending on the preferential adsorption of components of a solution percolated

through a tube of the gel, producing separate coloured bands (Zechmeister and Cholnoky, *Principles and Practice of Chromatography*, 1943). Colourless substances can also be separated, and other solids than alumina used.

Precipitated aluminium hydroxide adsorbs colouring matter and colloidal substances. With colours it forms *lakes* (which have been regarded as coordination compounds), and alum and aluminium salts are used as mordants in dyeing and in clarifying water and sewage. Fabrics are waterproofed (" rainproofs ") by steeping in aluminium acetate solution and steaming, when colloidal aluminium hydroxide is precipitated in the pores.

Definite crystalline *hydrates of alumina* are designated α and γ according as they give α- or γ-Al_2O_3 on dehydration (Lehl, *J. Phys. Chem.*, 1936, **40**, 47; Weiser, *Inorganic Colloid Chemistry*, 1935, **2**, 90; Laubengayer and Weisz, *J.A.C.S.*, 1943, **65**, 247).

Diaspore is α-Al_2O_3,H_2O and gives α-Al_2O_3 in steam at 400°. It is formed artificially by heating γ-Al_2O_3 and water under pressure at 430° and seeding with diaspore. *Böhmite* is γ-Al_2O_3,H_2O; it occurs in bauxite from Les Baux and is precipitated from a boiling solution of an aluminium salt by ammonia: it is the first product of the ageing of an amorphous gel and is stable in steam at 400°. *Bayerite* is γ-$Al_2O_3,3H_2O$, produced from böhmite gel by ageing under dilute alkali, is metastable at room temperature with respect to gibbsite but stable with respect to böhmite. *Gibbsite* or *hydrargillite* γ-$Al_2O_3,3H_2O$, the most stable form of the trihydrate, is found as a mineral and is formed from bayerite by long shaking with not too dilute alkali at 60°.

These compounds, the identity of which is confirmed by X-rays, are true hydroxides, diaspore and böhmite O=Al(OH), gibbsite and bayerite $Al(OH)_3$. *Bauxite*, formerly regarded as a dihydrate $Al_2O_3,2H_2O$, is a mixture (p. 416).

At a dull red heat the hydrates form Al_2O_3, which if produced at a relatively low temperature is soluble in acids but on strong heating becomes denser (2·8 at 600°, 3·9 at 1200°) and insoluble in acids. The change from γ-Al_2O_3 to α-Al_2O_3 occurs at about 850°, and the product can then be rendered soluble only by fusion with alkali hydroxide or bisulphate.

Colloidal aluminium hydroxide is known in two forms. (*a*) A solution of the precipitated hydroxide in aluminium chloride solution gives on dialysis a colloidal solution which acts as a mordant, forms lakes with dyes, and is coagulated by alkalis and salts, the precipitate being soluble in acids (Graham, 1861). (*b*) A solution of aluminium acetate kept for some time at 100°, the water which evaporates being replaced, loses all the acid and a second colloidal variety (*meta-aluminium hydroxide*) is formed, which does not form lakes or act as a mordant; it is precipitated by acids, alkalis, and salts, but the gel is sparingly soluble in acids (Crum, 1854). A milky colloidal solution is also formed by the action of 4 p.c. acetic acid on the well-washed precipitated hydroxide (Bentley and Rose, *J.A.C.S.*, 1913, **35**, 1490; Weiser, *J. Phys. Chem.*, 1920, **24**, 505).

Aluminium peroxide Al_2O_4 (?) mixed with alumina is precipitated by adding excess of 30 p.c. H_2O_2 to alumina dissolved in 30 p.c. potassium hydroxide solution (Terni, 1912).

Aluminates.—Aluminium hydroxide is amphoteric:

$$Al''' + 3OH' \rightleftharpoons Al(OH)_3 \rightleftharpoons H' + H_2AlO_3' \rightleftharpoons H' + AlO_2' + H_2O.$$

It dissolves in acids forming aluminium salts and acting as a base: $Al(OH)_3 + 3HCl \rightleftharpoons AlCl_3 + 3H_2O$. The reaction is reversible and the salts are hydrolysed by water, since aluminium hydroxide is a weak base. The hydroxide also dissolves in solutions of alkalis, acting as a weak acid and forming *aluminates* which are largely hydrolysed: $Al(OH)_3 + NaOH \rightleftharpoons NaAlO_2 + 2H_2O$. The acidic properties are weaker than the basic.

In solution only the **meta-aluminates** $MAlO_2$ appear to exist, since the freezing point of a solution of alkali is unaltered by dissolved alumina, so that an OH' ion is replaced by AlO_2': $OH' + Al(OH)_3 = AlO_2' + 2H_2O$ (Slade, 1911–12); at 18° $[H'][AlO_2'] = 1{\cdot}1 \times 10^{-15}$. **Potassium aluminate** $K_2Al_2O_4,3H_2O$ can be crystallised (Fremy, 1844; Allen and Rogers, *Amer. Chem. J.*, 1900, **24**, 304; Hawley, *J.A.C.S.*, 1907, **29**, 300; Goudriaan, *Rec. Trav. Chim.*, 1922, **41**, 82; Fricke and Jucaitis, 1930). If solutions of alumina in acid and alkali are mixed, the whole of the alumina may be precipitated: $Al''' + 3AlO_2' = 2Al_2O_3$. Solutions of aluminates are so largely hydrolysed: $NaAlO_2 + 2H_2O \rightleftharpoons Na' + OH' + Al(OH)_3$, that they may be titrated with acids like alkalis, and on standing alumina is slowly deposited. They do not appear to contain colloidal alumina, the slow deposition corresponding with a slow hydrolytic change. When boiled with alumina most of the aluminium hydroxide is precipitated. Sodium aluminate solution is used for water-softening (Clark and Cousins, *J.S.C.I.*, 1935, **54**, 143T).

Spinel Al_2MgO_4 and related compounds $Al_2[XO_4]$, where X = Be (*chrysoberyl*), Zn, Mn^{II}, Fe^{II}, Co, formerly regarded as aluminates, have aluminium in the cation. Aluminium cobaltate Al_2CoO_4 is contained in *Thenard's blue*, obtained by heating alumina with cobalt nitrate (blowpipe test for alumina). The compound $4CoO,3Al_2O_3$ is green (Hedvall, 1914).

Aluminium Halides

AlF_3, sublimes at 1291°. $AlCl_3$, m.p. 193°/2 atm., sublimes at 183°.
$AlBr_3$, m.p. 97·5°, b.p. 255°. AlI_3, m.p. 191°, b.p. 381°.

AlF_3 exists in hexagonal and rhombohedral, $AlCl_3$ in monoclinic and pseudo-hexagonal, and $AlBr_3$ in rhombohedral forms. The compounds are all colourless when pure.

Aluminium fluoride AlF_3 sublimes on heating aluminium strongly in hydrogen fluoride. It is scarcely soluble in water (0·5 g./100 g. H_2O) and is hardly attacked by boiling sulphuric acid. A solution of aluminium or the oxide or hydroxide in excess of hydrofluoric acid is strongly supersaturated and soon deposits hydrated AlF_3. The common hydrate $AlF_3,3\frac{1}{2}H_2O$ exists in two forms, one soluble and the other insoluble (Tosterud, *J.A.C.S.*, 1926, **48**, 1). $AlF_3,2H_2O$ occurs as the mineral *fluellite*. Aluminium fluoride dissolves in hydrofluoric acid, probably forming **fluoaluminic acid** H_3AlF_6, the sodium salt of which is the mineral cryolite Na_3AlF_6.

Cryolite, the only commercial natural source of which is Ivigtut in South Greenland, is used as a flux in the manufacture of aluminium. It has been used as a source of soda and alumina by Thomsen's process, worked from 1854.

Powdered cryolite (separated from gangue, etc., by an electromagnetic process) is heated with lime: $Na_3AlF_6 + 3CaO = 3CaF_2 + Na_3AlO_3$. The aluminate is dissolved out and decomposed by carbon dioxide.

$$2Na_3AlO_3 + 3H_2O + 3CO_2 = 3Na_2CO_3 + 2Al(OH)_3.$$

An artificial cryolite, free from silica, is made for use in the aluminium industry, *e.g.* by the reaction: $AlF_3 + 3NH_4F + 3NaNO_3 = Na_3AlF_6 + 3NH_4NO_3$ in solution.

Aluminium chloride $AlCl_3$ is obtained anhydrous as a sublimate by heating aluminium in a stream of dry chlorine: $2Al + 3Cl_2 = 2AlCl_3$, or in dry hydrogen chloride: $2Al + 6HCl = 2AlCl_3 + 3H_2$.

EXPT. 3.—Heat 10 g. of clean aluminium turnings in a hard-glass tube in a rapid stream of chlorine dried by concentrated sulphuric acid and collect the sublimate in a dry bottle, protected from heat by an asbestos screen (Fig. 194).

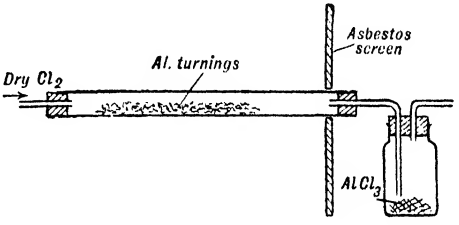


FIG. 194.—Preparation of aluminium chloride.

Aluminium chloride can be prepared from the oxide by two general methods which can be used to make several other anhydrous chlorides (including non-metal chlorides, such as those of boron and silicon):

(i) In the **Oersted process** (1825) an intimate mixture of the oxide and carbon is strongly heated in a stream of dry chlorine, when carbon monoxide and dioxide are also formed (Fischer and Gewehr, 1932):

$$Al_2O_3 + 3C + 3Cl_2 = 2AlCl_3 + 3CO.$$

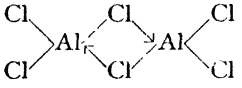
(ii) In the **Chauvenet process** (1911) a mixture of carbonyl chloride and chlorine is passed over the heated oxide:

$$Al_2O_3 + 3COCl_2 = 2AlCl_3 + 3CO_2.$$

Matignon used sulphur chloride S_2Cl_2 vapour instead of carbonyl chloride, when sulphur dioxide is formed. Carbon tetrachloride vapour has also been used.

Alumina is slowly decomposed when strongly heated alone in chlorine (Weber, 1861): $2Al_2O_3 + 6Cl_2 = 4AlCl_3 + 3O_2$, or when mixed with carbon and strongly heated in hydrogen chloride (Deville, 1855): $Al_2O_3 + 3C + 6HCl = 2AlCl_3 + 3CO + 3H_2$. Crude aluminium chloride for the petroleum industry is made by passing chlorine over a heated mixture of calcined bauxite and carbon at 870° (McAfee, *Ind. Eng. Chem.*, 1929, **21**, 670; Groggins, *ibid.*, 1931, **23**, 152; Simon, *Chim. et Ind.*, 1930, **24**, 1317). The chief use in the laboratory is in the Friedel-Crafts reaction in organic chemistry.

Anhydrous aluminium chloride is white when pure but is usually coloured yellow by ferric chloride as impurity. It is very hygroscopic and fumes in moist air. It sublimes at 183° without previous fusion (m.p. 193° at 2 atm.): the vapour density at 350°–400° corresponds with Al_2Cl_6 but diminishes with rise of temperature, and at 750°–800° it corresponds with $AlCl_3$ (Deville and Troost, 1857), remaining constant at higher temperatures: $Al_2Cl_6 \rightleftharpoons 2AlCl_3$. The formula for Al_2Cl_6:



and similar ones for Al_2Br_6 and Al_2I_6 are confirmed by electron diffraction (Palmer and Elliott, *J.A.C.S.*, 1938, **60**, 1852), the molecules having the form of two tetrahedra sharing an edge, and the coordination number of Al is 4.

With its ready volatility, solubility in organic solvents, and low conducting power when fused (the solid is a moderate conductor of electricity) aluminium chloride behaves as a covalent compound. The compound $Na[AlCl_4]$, formed by heating $AlCl_3$ and NaCl in a sealed tube, is a conductor when fused.

Anhydrous $AlCl_3$ combines with 1, 3, 5, 6, 7 and 14NH_3 (Klemm, etc., 1931), also with PH_3, H_2S, SCl_4, PCl_5, SO_2, NOCl, and many organic substances. With a little water a crystalline hydrate $AlCl_3,6H_2O$ is formed, more conveniently prepared by dissolving aluminium or soluble alumina in concentrated hydrochloric acid and saturating the solution with hydrogen chloride gas. It is hydrolysed in solution: $AlCl_3 + 3H_2O \rightleftharpoons Al(OH)_3 + 3HCl$ and can be titrated with alkali as if it were free hydrochloric acid. The hydrolysis is 0·72 p.c. in 0·1 molar and 1·97 p.c. in 0·01 molar solution (Čupr, 1931).

Aluminium bromide $AlBr_3$ (and Al_2Br_6) is formed by passing bromine vapour over heated aluminium in an inclined tube, from which the fused bromide can be collected. The vapour density at 400° corresponds with Al_2Br_6. There is a crystalline hydrate $AlBr_3,6H_2O$.

Aluminium iodide AlI_3 (and Al_2I_6) is prepared similarly to the bromide: the vapour density at the b.p. corresponds with 24 p.c. dissociation: $Al_2I_6 \rightleftharpoons 2AlI_3$. It reacts with carbon tetrachloride. $4AlI_3 + 3CCl_4 = 4AlCl_3 + 3CI_4$. There is a crystalline hydrate $AlI_3,6H_2O$.

Aluminium Compounds

Aluminium carbide Al_4C_3 is formed in yellow crystals by heating aluminium with carbon or from a mixture of aluminium oxide and carbon in the electric furnace (Moissan, 1895; Pring, *J.C.S.*, 1905, **87**, 1530; 1908, **93**, 2101). With water it forms methane (p. 451).

Since alumina is a very weak base no *carbonate* is known, but the basic double carbonate $Na(AlO)CO_3,H_2O$ occurs as *dawsonite*.

Aluminium silicates are of great importance in ceramic industries. The normal silicate $Al_2O_3,3SiO_2$ is unknown, but there are *basic silicates*. Three forms of Al_2O_3,SiO_2 are the rhombic *sillimanite* and *andalusite* and the triclinic *cyanite* (or *disthene*); *mullite*, rhombic, is $3Al_2O_3,2SiO_2$.

The first product of the weathering of felspar (p. 416) is " Cornish stone " in several varieties ; the next product is " china clay rock " which on washing forms " china clay." If the clay has been transported by water, glaciers, etc., it is called a " secondary clay " ; the purer varieties are more plastic than china clay and are called " ball clay."

Pure china clay (*kaolin* or *kaolinite*) is $Al_2O_3,2SiO_2,2H_2O$ (or $[Al_2O_3,2SiO_2]_2$, $3H_2O$). Other clay minerals are *halloysite* $Al_2O_3,2SiO_2$, 3 or $4H_2O$, *allophane* $Al_2O_3,SiO_2,4$, 5 or $6H_2O$ (soluble in hydrochloric acid, whilst kaolin is insoluble) and *montmorillonite* $Al_2O_3,4SiO_2,9H_2O$, present in fullers' earth and bentonite. Fullers' earth is " activated " for use as an adsorbent and for purifying oils by washing with hydrochloric acid, which removes alumina.

In making *pottery* and *porcelain* by heating (" firing ") clay the following changes occur. The clay first loses free and combined water. At 800°–1000° it shrinks, and above 1000° reaction occurs with formation of a mixture of silica as *cristobalite* (p. 499) and *mullite* : $3(Al_2O_3,2SiO_2) = 4SiO_2 + (3Al_2O_3,2SiO_2)$. At 1500° this sinters to a stony mass. This softens at 1650° and at 1740° fuses to a brown or grey viscous liquid.

The body of English earthenware is composed of ground Cornish stone, ground flint, china clay, and ball clay (added to confer plasticity). It is fired in an oxidising atmosphere at 1100°, and the " biscuit " body is then dipped in the " slip " of ground glaze and water, dried, and re-fired in a " glost-oven " at about 1500°. The *molar* composition of the glaze is :

$$\left.\begin{matrix}0{\cdot}4\ PbO\\0{\cdot}3\ CaO\\0{\cdot}3\ (K,Na)_2O\end{matrix}\right\}0{\cdot}28\ Al_2O_3\left\{\begin{matrix}3{\cdot}0\ SiO_2\\0{\cdot}5\ B_2O_3\end{matrix}\right. \quad \text{or} \quad \left.\begin{matrix}0{\cdot}3\ (K,Na)_2O\\0{\cdot}7\ CaO\end{matrix}\right\}0{\cdot}38\ Al_2O_3\left\{\begin{matrix}3{\cdot}8\ SiO_2\\0{\cdot}9\ B_2O_3\end{matrix}\right.$$

If the biscuit body has not received " under-glaze " decoration with suitable colours, the " on-glaze " decoration of mixtures of fusible frits containing silicates or borates and metallic oxides is applied to the glazed ware and fired in muffles at 800°–900°.

Hard porcelain is made from felspar, quartz and clay, baked at 900°, dipped in glaze (approximating in composition to felspar) and fired at 1400°–1600° in a reducing atmosphere, giving it a very faint bluish tinge. The mass undergoes partial fusion and is translucent. English " bone china " is made from bone ash, china clay and Cornish stone ; it is fired at 1200° in an oxidising atmosphere, the glaze is applied to the " biscuit," and the ware is re-fired at 1050°.

Earthenware *drainpipes*, etc., are salt-glazed (p. 305). *Bricks* are made from impure clay containing oxide of iron and fired at about 950°. A clay containing 1–3 p.c. of Fe_2O_3 is buff-coloured after firing, with 4–5 p.c. it is red. Yellow bricks are made from clay containing some chalk. Clay containing much silica and alumina in comparison with basic oxides (Na_2O,CaO) is *fireclay* (*e.g.* Stourbridge clay), used for refractory bricks : to prevent undue contraction on firing some broken firebrick (" grog ") is mixed with the clay. Crucibles are made from fireclay and coarse sand or ground burnt clay, and " plumbago " crucibles contain graphite.

Alumino-silicates have some silicon Si^{4+} replaced by aluminium Al^{3+} ions, and as the positive charge is thus reduced some alkali or alkaline earth metal

ions enter the lattice and make up the positive charge (see p. 505). An important group comprises the **felspars** and isomorphous mixtures of them, as follows :

Composition	Monoclinic		Triclinic	
	Pure	Isomorph. Mixture	Pure	Isomorph. Mixture
Potash felspar $K_2O,Al_2O_3,6SiO_2$	Orthoclase	Soda orthoclase	Microline	Anorthoclase
Soda felspar $Na_2O,Al_2O_3,6SiO_2$ -	Barberite		Albite	
Lime felspar $CaO,Al_2O_3,2SiO_2$ -	Unknown	—	Anorthite	Plagioclases

Celsian is monoclinic $BaO,Al_2O_3,2SiO_2$, which forms mixed crystals with orthoclase, Ba^{2+} replacing K^+, and Al^{3+} at the same time replacing Si^{4+} to balance the charges. *Carnegieite* is triclinic $Na_2O,Al_2O_3,2SiO_2$.

The general formula of a crystalline **zeolite** (excluding water) is $Al_xSi_yO_{2(x+y)}$ and for every $2Al^{3+}$ replacing Si^{4+}, two univalent or one bivalent cation enters the lattice. Common natural zeolites are *natrolith* $Na_2Al_2Si_3O_{10},2H_2O$, and *chabasite*, a mixture of $CaAl_2Si_6O_{16},8H_2O$ and $Ca_2Al_4Si_4O_{16},8H_2O$. Artificial zeolites used in base-exchange water softening (p. 676) apparently have the same composition as natural zeolites, *e.g.* $Na_2Al_2Si_3O_{10},4H_2O$, but are amorphous and glassy.

Ultramarine.—The rare dark blue mineral *lazurite* or *lapis lazuli* is a sodium aluminium silicate containing sulphur in forms not yet fully understood. The artificial form is *ultramarine*, obtained almost simultaneously and independently in 1826 by Guimet and Gmelin.

A mixture of kaolin, soda-ash or sodium sulphate, sulphur, and resin or wood charcoal is heated to redness in a closed crucible. A **white ultramarine** is formed in complete absence of air, but when air is admitted a **green ultramarine** is formed. If this or white ultramarine is mixed with powdered sulphur and heated in air the commercial **blue ultramarine** is formed, which is ground and washed. If this is heated in a stream of dry chlorine, nitric oxide, or hydrogen chloride, a **violet** and finally a **red ultramarine** result. The sodium may be replaced by its equivalent of silver by treatment with silver nitrate and a yellow **silver ultramarine** obtained.

Alkalis have no action on ultramarine, so that it can be used in laundering as it is not attacked by soap or soda. Acids rapidly decompose it with evolution of hydrogen sulphide and a white gelatinous residue remains. Fuming sulphuric acid does not produce this change.

The ultramarines have been variously formulated, *e.g.* :

	Brögger and Bäckström (1891)	R. Hoffmann (1873)
White - - -	$Na_6Al_3Si_3SO_{12}$	$Na_{10}Al_6Si_6S_2O_{24}$
Green - - -	$Na_6Al_3Si_3S_2O_{12}$	$Na_8Al_6Si_6S_2O_{24}$
Blue - - -	$Na_6Al_3Si_3S_3O_{12}$	$Na_7Al_6Si_6S_2O_{24}$

According to Hoffmann lapis lazuli is $Na_{10}Al_6Si_6S_6O_{24}$ and blue ultramarines richer in sulphur are $Na_8Al_6Si_6S_4O_{24}$ and $Na_6Al_4Si_6S_4O_{20}$. The violet ultramarine

is perhaps a mixture of the blue and red. Silver ultramarine has been formulated $Ag_6Al_6Si_6S_3O_{30}$ and potassium and lithium chlorides are said to give with it the corresponding K and Li ultramarines; these may be zeolitic base-exchange reactions.

A relation between lapis lazuli (lazurite) and other minerals of a zeolite-like character, *noseane* $3Na_2Al_2Si_2O_8,Na_2SO_4$ and *hauyne* $3Na_2Al_2Si_2O_8,2CaSO_4$, derived from *nepheline* $Na_2Al_2Si_2O_8$, was long suspected and is confirmed by X-ray analysis, whilst the structure of *sodalite* $3Na_2Al_2Si_2O_8,2NaCl$ is different (Jaeger, *Trans. Faraday Soc.*, 1929, **25**, 320, who formulates blue ultramarine as $Na_6Al_4Si_6S_3O_{24}$).

Podschus, Hofmann and Leschewski (*Z. anorg. Chem.*, 1936, **228**, 305) modified and simplified the structure proposed by Jaeger, and find that the sulphur exists partly ionic and partly as S_2 molecules. The basis of the structure is a body-centred cubic lattice and the unit cell contains 24O, 6Si and 6Al atoms, this unit $[Al_6Si_6O_{24}]^{6-}$ (which is found in Hoffmann's formula given above) forming a regular octahedral group in the Si,Al,O skeleton, with wide spaces characteristic of the zeolites. There is room only for eight large sodium cations and a new analysis gave $Na_{6\cdot63}Al_{5\cdot87}Si_{6\cdot13}O_{24}S_{2\cdot45}$. It is supposed that the sodium ions are distributed statistically over the available spaces and the S_2 groups are put into octahedral groups at the centre and corners, not more than two of the six possible positions being occupied. For further details the original must be consulted.

Aluminium nitride AlN is formed as a powder of hexagonal crystals by heating aluminium powder in nitrogen at 740° (Neumann, Kröger, and Haebler, 1932). The impure nitride formed by heating a mixture of bauxite and carbon in a stream of nitrogen at 1600°: $Al_2O_3 + 3C + N_2 = 2AlN + 3CO$, when heated in a stream of nitrogen in a carbon tube at 2020° gives a sublimate of colourless hexagonal needles of pure nitride. Aluminium nitride evolves ammonia with hot dilute alkali: $2AlN + 3H_2O = Al_2O_3 + 2NH_3$. This was the basis of the obsolete *Serpek process* for the utilisation of atmospheric nitrogen.

Aluminium nitrate is not known anhydrous; the hydrate $Al(NO_3)_3,9H_2O$ is formed by mixing solutions of aluminium sulphate and lead nitrate, filtering and evaporating. Hydrates with 8, 6 and $4H_2O$ are also known. The salt, which hydrolyses, is used as a mordant and in making gas mantles.

Aluminium phosphide AlP (cubic) is formed from the elements on heating.

Aluminium phosphate $AlPO_4$ is formed as a gelatinous precipitate, soluble in mineral acids and alkalis (it is decomposed by ammonia) but not in acetic acid, on adding a neutral solution of an aluminium salt to sodium phosphate solution (Caven and Hill, *J.S.C.I.*, 1897, **16**, 29). The basic phosphate is the mineral *wavellite* $(AlOH)_3(PO_4)_2,5H_2O$; *turquoise* is $Al_2(OH)_3PO_4,H_2O$ in which part of the Al_2 is replaced by Cu^{II}_3 and Fe^{II}_3 (causing the blue colour) and Ca_3. *Lazulite*, a rare blue mineral, is $(Mg,Ca,Fe^{II})(AlOH)_2(PO_4)_2$: it must not be confused with *lazurite* or lapis lazuli.

Aluminium sulphide Al_2S_3 (cubic) is formed by adding sulphur to fused aluminium (a mixture of the powders may explode on heating), by passing sulphur or carbon disulphide vapour over a strongly heated mixture of alumina and carbon: $Al_2O_3 + 3C + 3S = Al_2S_3 + 3CO$, and by heating a mixture of Al-Sb alloy with

Sb_2S_3 in vacuum at 1000° (Picon, 1929). When nearly pure it is yellow; it sublimes at high temperatures. Since it is completely hydrolysed by water, only aluminium hydroxide is precipitated by ammonium sulphide from a solution of an aluminium salt: $Al''' + 3HS' + 3H_2O = Al(OH)_3 + 3H_2S$.

Aluminium sulphate.—On slow cooling, a solution of alumina in hot concentrated sulphuric acid deposits an indistinctly crystalline mass of $Al_2(SO_4)_3,17$ or $18H_2O$ (Smith, *J.A.C.S.*, 1942, **64**, 41), which is purified by dissolving in a little water and adding alcohol, when the oily supersaturated solution first separating soon solidifies to lustrous scaly crystals. On heating, these intumesce, leaving a white mass of anhydrous sulphate, which decomposes at 600° (nearly completely at 800°) into Al_2O_3, SO_3, SO_2 and O_2 (Cobb, *J.S.C.I.*, 1910, **29**, 250): $Al_2(SO_4)_3 = Al_2O_3 + 3SO_3$. Hydrates with 27, 16, 12 (?), 10, 6 and 2 (?) H_2O are described (Krauss and Fricke, 1927).

Commercial aluminium sulphate (14–15 or 17–18 p.c. Al_2O_3) is made by heating bauxite with diluted sulphuric acid or kaolin with concentrated sulphuric acid:

$$Al_2O_3,2SiO_2,2H_2O + 3H_2SO_4 = Al_2(SO_4)_3 + 2SiO_2 + 5H_2O.$$

A crude mixture (*alumino-ferric*) of aluminium and ferric sulphates (which cannot be separated by crystallisation) made from bauxite is used in purifying sewage (the modern products may contain only 0·5 p.c. of ferrous iron). If the ferric is reduced to ferrous sulphate (*e.g.* by H_2S) the aluminium sulphate may be crystallised; the iron may also be precipitated as Prussian blue or as sulphide.

Pure aluminium sulphate (or alum) mixed with sodium bicarbonate is used in American baking powder but is forbidden in Great Britain:

$$Al_2(SO_4)_3 + 6NaHCO_3 = 2Al(OH)_3 + 3Na_2SO_4 + 6CO_2.$$

Precipitated aluminium hydroxide dissolves in aluminium sulphate solution and a basic salt $Al_2O_3,2SO_3,12H_2O$ or $Al_2(OH)_2(SO_4)_2,11H_2O$ deposits; this occurs as the Spanish mineral *alumian*. The mineral *websterite* (used in making alum) is $Al_2O_3,SO_3,9H_2O$ or $Al_2(OH)_4SO_4,7H_2O$; $Al_2(SO_4)_3,17H_2O$ occurs as *halotrichite* or *feather alum* in Bohemia, Chile, etc.

Alums.—The name *alum* is given to double salts of the type $M^IM^{III}(SO_4)_2$, $12H_2O$, where:

M^I (*univalent*) may be Li, Na, K, NH_4, Rb, Cs, NH_4O (hydroxylaminium), Tl, or the radical of a quaternary nitrogen base such as $N(CH_3)_4$,

M^{III} (*tervalent*) may be Al, Ga, In, Ti, V, Cr, Mn, Fe, Co, Rh. (Rare earths do not form alums.) The selenate radical SeO_4 may replace SO_4, and alums $M^I_2SO_4$, $M^{III}_2(SO_4)_3,24H_2O$ are isomorphous with $K_2BeF_4,Al_2(SO_4)_3,24H_2O$ (Curjel, 1929). The alums crystallise in octahedra.

The X-rays show (Lipson, *Nature*, 1935, **135**, 912; *Proc. Roy. Soc.*, 1935, **148**, 664; **151**, 347) that the different alums have really three different structures depending on the size of the alkali metal ion: α (medium size, Rb), β (large, Cs), and γ (small, Na). The different forms do not give solid solutions but appear separately on crystallisation.

The solubilities of alums in g. $MAl(SO_4)_2,12H_2O$ in 100 g. H_2O are :

	0°	20°	30°	40°	50°	80°	100°
Na - -	106·4	116·5	126·5	turbid above 40°		—	—
K - -	5·7	12·0	18·49	25·00	36·78	84·0	136·9
NH_4 -	3·9	15·13	22·01	30·92	44·10	67·2	135·3

Lithium alum crystallises only below 0° (J. F. Spencer and Oddie, *Nature*, 1936, **138**, 169 ; Horan and Duane, *J.A.C.S.*, 1941, **63**, 3533). **Sodium alum** is very soluble and difficult to prepare : it is stable only between 11° and 39° and effloresces in air (Smith, *J.A.C.S.*, 1909, **31**, 245 ; Dobbins and Byrd, *J. Phys. Chem.*, 1931, **35**, 3673).

Potassium and **ammonium alums** readily crystallise in octahedra and hence (unlike aluminium sulphate) are easily purified by crystallisation. They are made by crystallising a hot concentrated solution of aluminium and alkali sulphates. They are now largely replaced in industry by purified aluminium sulphate.

Potash alum was formerly made by roasting *alunite* $KAl_3(OH)_6(SO_4)_2$ with coal, exposing to air, lixiviating and crystallising :

$$KAl_3(OH)_6(SO_4)_2 = KAl(SO_4)_2 + Al_2O_3 + 3H_2O.$$

As so prepared it is called *Roman alum* (as it was made at Tolfa, near Civita-vecchia, in a works belonging to the Pope), and although pink from the presence of ferric oxide it was free from soluble iron salts, which give dull colours to lakes in mordanting. For the more delicate dyes the alum must contain less than 0·01 p.c. of iron.

Alum crystallises in cubes from weakly alkaline solutions and Roman alum is cubic. In the modern process the calcined alunite is treated with sulphuric acid and potassium sulphate added to the solution.

On adding potassium hydroxide to alum solution until the precipitate of alumina just no longer dissolves completely on stirring, a solution of " neutral alum " is formed ; at 40° this precipitates a basic salt of the same composition as alunite.

Potassium alum seems to effloresce in air but actually ammonia is absorbed and a basic salt formed. It melts at 92° and loses all the water of crystallisation at 200°, forming a white porous mass of " burnt alum." Ammonium alum melts at 95° and on heating loses ammonia and sulphuric acid, leaving a residue of pure alumina at a red heat :

$$(NH_4)_2SO_4,Al_2(SO_4)_3,24H_2O = 2NH_3 + 4H_2SO_4 + Al_2O_3 + 21H_2O.$$

Gallium

The rare element **gallium** occurs in minute traces in most specimens of zinc blende, and was discovered by the spectroscope in a blende from Pierrefitte by Lecoq de Boisbaudran in 1875. It is the *eka-aluminium* of Mendeléeff. Gallium occurs in traces in bauxite and in commercial aluminium, in the residues of zinc distillation (Hillebrand, *Ind. Eng. Chem.*, 1916, **8**, 225), in some coal ash (Morgan and Davies, *J.S.C.I.*, 1937, **56**, 717), and in the mineral germanite (Sebba and

Pugh, *J.C.S.*, 1937, 1371). It is now extracted from the by-products of the Mansfeld copper schist (Einecke, *Das Gallium*, Leipzig, 1937). Middlesborough cast iron contains 1 part of gallium in 33,000.

The metal is deposited by electrolysis of an alkaline solution of a salt. Gallium is hard and brittle ; it has a low m.p. 29·78° and remains persistently superfused, so that it is often liquid at room temperature. The metal (or an alloy with tin and indium of lower m.p.) has been proposed for high temperature thermometers.

Gallium is stable in dry air and does not decompose water. It dissolves in concentrated hydrochloric acid, but (like aluminium) is only slowly attacked by nitric acid : it evolves hydrogen with alkalis and is vigorously attacked by halogens.

A volatile **gallium hydride** Ga_2H_6 (m.p. $-21{\cdot}4°$, decomposes at 130°) is formed by the action of triethylamine on the methyl derivative (Wiberg and Johannsen, 1942) : $3Ga_2H_2(CH_3)_4 + 4N(C_2H_5)_3 = Ga_2H_6 + 4Ga(CH_3)_3 \cdot N(C_2H_5)_3$. The compound $Ga_2H_2(CH_3)_4$ is made by passing $Ga(CH_3)_3$ vapour and hydrogen through a glow discharge.

Gallium is normally tervalent but sometimes apparently bivalent ($GaCl_2$, $GaBr_2$, GaI_2, GaS) and univalent (Ga_2O, Ga_2S). Since the bivalent compounds are diamagnetic they are probably complex and contain uni- and tervalent gallium : $Ga^I[Ga^{III}Cl_4]$, etc. The **trichloride** $GaCl_3$, m.p. 78°, b.p. 205°, is a white solid formed by burning the metal in chlorine ; at 498° the vapour is largely associated to Ga_2Cl_6 (Laubengayer and Schirmer, *J.A.C.S.*, 1940, **62**, 1578). The trichloride is extracted from hydrochloric acid solution by ether. When heated with the metal at 200° $GaCl_3$ forms the white **dichloride** $GaCl_2$, m.p. 164°, b.p. 535°. **Gallium sesquioxide** Ga_2O_3, which (like Al_2O_3) exists in different forms, m.p. 1740°, is formed as a white solid on burning the metal in air or oxygen ; when heated at 700° with the metal it forms the brown **suboxide** Ga_2O, which reduces cold dilute sulphuric acid to hydrogen sulphide. The **hydroxide** $Ga(OH)_3$ is formed as a white gelatinous precipitate by ammonia and a gallium salt : like alumina it is amphoteric and dissolves in acids and alkalis : solid *metagallates* MGa_2O_4 of beryllium, magnesium and zinc are formed on heating the mixed oxides at 1000°. The yellow **sulphide** Ga_2S_3 is formed by heating the metal in sulphur vapour : it is decomposed by water and when heated in hydrogen forms yellow GaS, stable to water, which in vacuum at 700° gives Ga_2S, only slowly attacked by water. The soluble **sulphate** $Ga_2(SO_4)_3,16H_2O$ readily forms alums. A dark grey **nitride** GaN is formed on heating gallium in ammonia at 1000° ; it is stable to air, water and dilute acids. No carbonate is known, alkali carbonates precipitating only the hydroxide (cf. Al).

Indium

Indium was discovered by the spectroscope by Reich and Richter in 1863 in a zinc blende from Freiberg : it gives a dark blue flame coloration. Indium occurs in all commercial tin (Garrett, *Proc. Roy. Soc.*, 1927, **114**, 289) and the Bolivian mineral *cylindrite* contains 0·1–1 p.c. (Brewer and Baker, *J.C.S.*, 1936, 1286, 1290 ; Lawrence and Westbrook, *Ind. Eng. Chem.*, 1938, **30**, 611). The metal is precipitated from solution by zinc and purified electrolytically. It has been used in plating silver to prevent tarnish. It is soft, not attacked by air or boiling water, soluble in cold concentrated sulphuric or hydrochloric acid, and also in alkali with evolution of hydrogen. It burns when strongly heated in air to the yellow **oxide** In_2O_3, which is easily reduced to the metal.

Indium is normally tervalent but there are compounds ($InCl, In_2O$) in which it is univalent and halides in which it is apparently bivalent: the latter are probably complex, *e.g.* In_2Cl_4 or $In^I[In^{III}Cl_4]$, containing uni- and tervalent indium, as they are diamagnetic. The **trichloride** $InCl_3$ is formed when the metal burns in chlorine and has the normal vapour density. The gelatinous **hydroxide** $In(OH)_3$ is precipitated by ammonia even in presence of tartaric acid: it is insoluble in ammonia but soluble in alkali hydroxide to a solution which quickly becomes turbid, and it forms $Mg(InO_2)_2,3H_2O$, so that it has some acidic character. The black **sub-oxide** In_2O is formed by heating In_2O_3 in hydrogen at 500°. The **sulphides** are In_2S_3 (red and yellow forms), InS and In_2S, the **sulphate** $In_2(SO_4)$ forms alums, and the **carbonate** $In_2(CO_3)_3$ is precipitated, together with hydroxide, by alkali carbonate.

Thallium

In 1861 Crookes observed a bright green line in the spectrum of flue dust from a vitriol works, which he attributed to a new element. The metal was independently discovered and first isolated in quantity by Lamy in 1862. Crookes gave it the name thallium from the Greek *thallos*, a young twig, on account of the colour imparted to a flame. The only minerals rich in thallium are *crookesite* (17 p.c. Tl, with Se, Cu, Ag), and *lorandite* $TlAsS_2$.

Thallium may be obtained from flue dust or pyrites by dissolving in aqua regia, evaporating, precipitating with hydrogen sulphide and then ammonia in the usual group separations, and then adding potassium iodide to the filtrate. A yellow precipitate of thallous iodide TlI is formed which gives a green coloration when heated on platinum wire in a Bunsen flame. If this is reduced with zinc and dilute sulphuric acid the metal is obtained; the chloride is also reduced on fusion with sodium carbonate and potassium cyanide (Sisson and Edmonson, *J.S.C.I.*, 1919, **38**, 70T).

Thallium is greyish-white and soft like lead, m.p. 303·5°, b.p. 1475°; the vapour is monatomic. It oxidises in moist air, decomposes steam at a red heat, and dissolves readily in dilute sulphuric acid and especially in dilute nitric acid. It is less easily soluble in hydrochloric acid, since thallous chloride TlCl is sparingly soluble. Thallium compounds are poisonous, and thallous sulphate is used as an ant-exterminator (*J.S.C.I.*, 1933, **52**, 687R).

Thallium forms **thallous compounds** TlX in which it is univalent and shows analogies with alkali metals, silver, and sometimes lead (thallous iodide TlI resembles lead iodide PbI_2), and **thallic compounds** TlX_3 in which it is tervalent and shows analogies with gold, aluminium and ferric iron. The thallic compounds are essentially covalent.

On evaporating a solution of thallium in dilute sulphuric acid, crystals of **thallous sulphate** Tl_2SO_4, isomorphous with potassium sulphate and forming an alum $TlAl(SO_4)_2,12H_2O$ are obtained. From its solution hydrochloric acid precipitates white **thallous chloride** TlCl, resembling silver chloride in becoming violet on exposure to light, but sparingly soluble in ammonia. With chloroplatinic acid a sparingly soluble **chloroplatinate** Tl_2PtCl_6, resembling K_2PtCl_6, is formed. Iodides precipitate yellow **thallous iodide** TlI, almost insoluble in cold water but dissolving in 830 parts of boiling water (cf. PbI_2).

Thallous hydroxide TlOH is obtained in yellow needles by decomposing a solution of thallous sulphate with baryta water, filtering, and evaporating. The solution is alkaline, and turns turmeric paper brown, but then bleaches it. If

heated out of contact with air at 100° TlOH forms black **thallous oxide** Tl_2O, dissolving in water to form a colourless solution of TlOH.

Thallous hydroxide solution absorbs carbon dioxide, forming the soluble **thallous carbonate** Tl_2CO_3, the solution of which is hydrolysed (cf. K_2CO_3).

Hydrogen sulphide gives with alkaline solutions of thallous salts a black precipitate of **thallous sulphide** Tl_2S, soluble in dilute acids (except acetic) but insoluble in ammonium sulphide.

Thallic chloride $TlCl_3,4H_2O$ is formed by passing chlorine into a suspension of thallous chloride in water and evaporating at 60°.

On addition of hydrogen peroxide, or bromine and alkali, a solution of thallous hydroxide gives a brown precipitate of **thallic hydroxide** $Tl(OH)_3$ or $TlO(OH)$, which loses water on heating and forms brown **thallic oxide** Tl_2O_3 (cf. Pb_2O_3). This dissolves in concentrated hydrochloric acid to form a solution of thallic chloride $TlCl_3$ (Berry, *J.C.S.*, 1922, **121**, 394; 1923, **123**, 1109). Thallic oxide is also formed by burning thallium in oxygen.

Thallic sulphide Tl_2S_3 is a black pitch-like mass obtained by fusing thallium with excess of sulphur. **Thallic sulphate** $Tl_2(SO_4)_3,7H_2O$, formed by dissolving thallic oxide in dilute sulphuric acid, is decomposed by water with precipitation of a basic salt $Tl(OH)SO_4,2H_2O$, and forms with potassium sulphate a compound $K_2SO_4,Tl_2(SO_4)_3,8H_2O$ which is not a true alum.

Thallium tri-iodide TlI_3, formed in splendid black crystals by digesting TlI with a solution of iodine in alcohol and evaporating, is not a thallic compound but a thallous polyiodide $TlI{\cdot}I_2$, isomorphous with RbI_3 and CsI_3 (Wells and Penfield, 1894).

An oxide Tl_2O_5 is said to be deposited on the anode in the electrolysis of a solution of Tl_2SO_4 faintly acidified with oxalic acid.

In its analogies to the alkali metals, lead and aluminium, thallium shows a greater diversity of properties than most other elements: Dumas (1863) appropriately called it the "ornithorhynchus among the metals"—the duckbill platypus. Thallium is used to a limited extent in the production of a very refractive optical glass, obtained by fusing the carbonate with sand and red lead. It is used, probably as oxysulphide, in the so-called "thalofide" photoelectric cells.

The Rare Earths

The substances known as the **rare earths** are the basic oxides of metals which all belong to the third group of the Periodic System. The general formula is M_2O_3, but the common oxide of cerium is CeO_2 and there are oxides PrO_2, Pr_4O_7 (or Pr_6O_{11}) and Tb_4O_7. The rare earths occur in rare minerals in the Urals, Scandinavia, Greenland, the United States (Idaho and Texas) and Brazil, usually as silicates in granite rocks.

Examples of rare earth minerals are: *cerite* $H_3(Ca,Fe)Ce_3Si_3O_{13}$, *orthite* (or *allanite*) $Al(OH)Ca_2(Al,Fe,Ce)_2(SiO_4)_3$, *gadolinite* $FeBe_2Y_2Si_2O_{10}$, *xenotime* YPO_4, *fergusonite* $YNbO_4$, *Australian fergusonite* $YTaO_4$, *euxenite*, *polycras*, *blomstrandite* and *priorite*, also containing Nb, Ta and Ti, *samarskite*, also containing U, Th, Nb and Ta, and its variety *yttrotantalite* $Y_4(Ta_2O_7)_3$, and *monazite*, containing phosphates of cerium and lanthanum (p. 534) and found in India, Brazil and Carolina. Each usually contains a number of earths. Cerite contains lanthanum, praseodymium, neodymium, samarium, cerium and traces of other earths; gadolinite contains chiefly yttrium, erbium, etc., with only small amounts of cerium and lanthanum.

The rare earths are usually divided into two groups :

I. **Cerite earths** : oxides of cerium, lanthanum, praseodymium, neodymium, samarium and europium. (The existence of illinium in the group is now doubtful.)

II. **Gadolinite earths** : oxides of scandium, yttrium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium and lutecium.

Separation of the rare earths.—The rare earth elements resemble one another very closely and are very difficult to separate. They are precipitated by oxalic acid in *acid* solution, and the oxides are formed by heating the oxalates. The principal methods of separation (Levy, *The Rare Earths*, 1924) comprise :

(1) Fractional decomposition of the nitrates by heat.

(2) Fractional precipitation with bases.

(3) Fractional crystallisation of salts and double salts with ammonium nitrate, bismuth nitrate, etc. (the usual method).

(4) Fractional precipitation of salts with oxalic acid, succinic acid, potassium stearate, etc.

A fractional crystallisation is represented diagrammatically by Fig. 195. A large quantity of solution is allowed to crystallise and six (say) crops of crystals are removed in succession, represented by the top row of black dots, leaving a mother-liquor represented by S_1. Each crop is now recrystallised, giving a solid and a mother-liquor represented by dots and circles on the second line.

The mother-liquor from crop 1 is combined with the crystals from crop 2, the mother-liquor from crop 2 with the crystals from crop 3, and so on. The solutions so formed are again allowed to crystallise and the fractions of the third row are obtained, and so the process goes on.

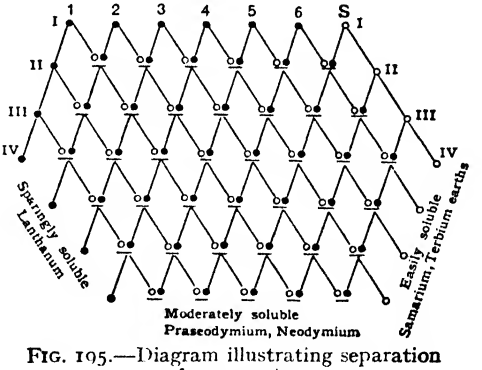


FIG. 195.—Diagram illustrating separation of rare earths.

As an example the separation of the supposed single earth didymia into two, praseodymia and neodymia, by Auer von Welsbach in 1885 may be quoted. The " didymium " salts were colourless but in solution showed absorption bands in the green and red. By repeated crystallisation of the double sodium and ammonium nitrates from nitric acid two fractions were obtained, one green (*praseodymium* salt) and the other rose-coloured (*neodymium* salt), showing separately the two parts of the absorption spectrum of the original substance. The colours are complementary and the mixture, like a mixture of cobalt and nickel salts, is colourless. Since neodymia and praseodymia nearly always occur with other earths, the absorption bands, even in the spectrum of light reflected from the sand or native earth, is an indication of rare earths. In the separation of ytterbium and lutecium, Urbain used 15,000 crystallisations.

The progress of the separation may be controlled by the examination of various types of spectra : flame, arc, spark, absorption and X-ray, and the rare earth compounds usually give pronounced and characteristic lines and bands, many being coloured. The cathode ray phosphorescence spectra studied by Crookes are due to traces of impurities. The X-ray spectra are particularly important in having settled the number and individuality of the rare earth elements, only one (at. no. 61) being now doubtful.

Chemical properties of the rare earths.—Since the rare earth elements are so closely alike, it is possible to give an accurate *general* description of their chemical properties.

The rare earths occupy a place between the strongly basic alkaline earths and weakly basic alumina, the least basic being scandium oxide and the most basic lanthanum oxide, which absorbs carbon dioxide from the air. The salts are not usually hydrolysed in solution. Some salts and oxides are coloured. The colours of salts are :

(*a*) Ce^{IV} orange, Pr green, Nd red-violet, Sm topaz-yellow, Eu pale rose.

(*b*) Tb rose, Dy bright green, Ho rose, Er deep rose, Tm bluish-green.

Salts of other rare earth elements are colourless. Traces of a coloured oxide may give an intense colour to a white oxide : 1·5 p.c. of terbium oxide renders gadolinium oxide ochre-brown.

The **metals** are obtained by the electrolysis of the chlorides, or by heating the chlorides with alkali metals (Klemm and Bommer, 1937). They are yellowish-white, brilliant and fairly resistant in air. On heating they absorb hydrogen or nitrogen, forming hydrides (*e.g.* LaH_3) or nitrides (*e.g.* LaN). Metallic cerium mixed with lanthanum and other rare earth metals is obtained by the electrolysis of the chlorides of the metals in the residues from the extraction of thorium from monazite (p. 534). The mixture, called " mixed metal," is used in alloy with iron in automatic lighters, since when abraded it throws off showers of hot sparks which will kindle coal gas or petrol vapour.

The **hydroxides** are precipitated by alkali and are insoluble in excess : lanthanum hydroxide turns moist red litmus paper blue and (also the oxide) absorbs carbon dioxide from the air. The **oxides**, generally M_2O_3, are obtained by heating the nitrates, hydroxides or oxalates in air. They are mostly amorphous and dissolve in dilute acids even after ignition. On addition of hydrogen peroxide and alkali, **peroxide hydrates** $(HO)_2MO{\cdot}OH$ are precipitated from solutions of the salts.

The anhydrous **chlorides** MCl_3 are obtained by heating the oxides in a stream of chlorine mixed with carbonyl chloride or sulphur chloride vapour. They are non-volatile and soluble in water, alcohol and pyridine. Lower chlorides (reducing agents) are $SmCl_2$, $EuCl_2$ and $YbCl_2$. The **sulphides** M_2S_3 (also La_2S_4 and Pr_2S_4) are hydrolysed by water and are prepared by dry methods, *e.g.* heating the anhydrous sulphates in hydrogen sulphide. The **sulphates** $M_2(SO_4)_3$ do not form alums ; those of the gadolinite earths usually crystallise with $8H_2O$. The **nitrates** $M(NO_3)_3$ usually crystallise with $6H_2O$ and are isomorphous with bismuth nitrate. Since the rare earths (except scandium oxide) are fairly strong bases they form normal **carbonates** $M_2(CO_3)_3$.

Cerium forms two series of compounds, the **cerous** CeX_3 and **ceric** CeX_4. The cerous salts are stable and colourless, usually similar in composition to and isomorphous with the corresponding compounds of other rare earth elements.

Cerium dioxide CeO_2, the stable oxide, contains quadrivalent cerium, and **cerous oxide** Ce_2O_3 is obtained by reduction of the dioxide with calcium. **Cerous hydroxide** $Ce(OH)_3$ is formed as a white precipitate on addition of alkali to solutions of cerous salts but is rapidly oxidised by air, becoming red and violet and finally pure yellow when **ceric hydroxide** $Ce(OH)_4$ is produced.

Cerium dioxide is a white powder with a faint yellow tinge if traces of praseodymium are present, and the commercial oxide is usually yellowish-brown. It is used in gas mantles (p. 534). A yellow solution of **ceric sulphate** $Ce(SO_4)_2$, made by dissolving CeO_2 in sulphuric acid, is an oxidising agent and is used in volumetric analysis.

Atomic structure of rare earth elements.—The peculiar position of the rare earth elements in the Periodic Table and their chemical properties were explained by Bohr on the assumption that the 4_4 quantum level * is empty as far as lanthanum, the electrons going into the higher levels 5_1, 5_2, 5_3 and 6_1 by preference, since some of these represent lower energies (p. 260). Only when these are partly filled does the 4_4 level begin to fill up, and as this requires 14 electrons to complete the group of 32 in all the 4-quantum levels, there will be 15 rare earth elements from lanthanum to lutecium, inclusive. Each has the same external electron configuration and hence very similar chemical properties, and the atoms differ only in the nuclei and the number of electrons in the deep inner 4-quantum level. The table gives the electronic structures of the atoms, including hafnium, an element in which the 5_3 level now contains two electrons which, with the two electrons in the 6_1 level, make it quadrivalent, so that it is not a rare earth element but belongs to Group IV.

	1_1	2_1+2_2	$3_1+3_2+3_3$	4_1	4_2	4_3	4_4	5_1	5_2	5_3	5_4	5_5	6_1
La -	2	8	18	2	6	10	0	2	6	1	0	0	2
Ce -	2	8	18	2	6	10	1	2	6	1	0	0	2
Pr -	2	8	18	2	6	10	2	2	6	1	0	0	2
Nd -	2	8	18	2	6	10	3	2	6	1	0	0	2
61 -	2	8	18	2	6	10	4	2	6	1	0	0	2
Sm -	2	8	18	2	6	10	5	2	6	1	0	0	2
Eu -	2	8	18	2	6	10	6	2	6	1	0	0	2
Gd -	2	8	18	2	6	10	7	2	6	1	0	0	2
Tb -	2	8	18	2	6	10	8	2	6	1	0	0	2
Dy -	2	8	18	2	6	10	9	2	6	1	0	0	2
Ho -	2	8	18	2	6	10	10	2	6	1	0	0	2
Er -	2	8	18	2	6	10	11	2	6	1	0	0	2
Tm -	2	8	18	2	6	10	12	2	6	1	0	0	2
Yb -	2	8	18	2	6	10	13	2	6	1	0	0	2
Lu -	2	8	18	2	6	10	14	2	6	1	0	0	2
Hf -	2	8	18	2	6	10	14	2	6	2	0	0	2

Owing to the incomplete inner 4_4 levels from La to Yb, the rare earth compounds are (i) often coloured and (ii) paramagnetic, and they are *transitional elements* in the wider sense. The ions Sc^{+++}, Y^{+++}, La^{+++}, Ce^{++++} and Lu^{+++} are, however, not paramagnetic, since they either have no 4_4 electrons at all or else, in the case of Lu^{+++}, have a complete 4_4 group. In the case of Ce^{++++} the single 4_4 electron has functioned as a valency electron and has been removed.

* Bohr's notation for the quantum numbers (p. 257) is used here.

The ions of the elements from Ce^{+++} to Yb^{+++} possess 4_4 electrons and are paramagnetic. The " active " electrons, causing colour, present in the 4_4 levels are partly screened by the completed 5_1 and 5_2 levels, and except in the case of cerium do not function as valency electrons. The *densities* of the oxides increase with the atomic weight from La to Lu, whereas in the group Sc, Y and La the density decreases with increasing atomic weight. The decrease in *atomic volume* in the series La to Lu is called the *lanthanide contraction* and has a theoretical explanation (p. 262).

The radii in A. of the 3-valent ions are :

Sc 0·83 Y 1·06.

La 1·22 Ce 1·18 Pr 1·16 Nd 1·15 — Sm 1·13 Eu 1·13

Gd 1·11 Tb 1·09 Dy 1·07 Ho 1·05 Er 1·04 Tu 1·04 Yb 1·00 Lu 0·99.

With Sc and Y (non-lanthanide) there is an *expansion* of 0·23A, whilst in passing from La to Lu (lanthanide) there is a total *contraction* of 0·23A. The introduction of an electron into the 4_4 (or $4f$) level, deep within the atom, produces only a negligible effect, whilst the increasing nuclear charge exerts an increasing attraction on the outer valency electrons (the same in all the elements from La to Lu) and hence gives rise to a contraction, in the lanthanide series. The elements Sm to Gd resemble La, Tb and Ho resemble Y, and Yb and Lu resemble Sc, and these groups usually occur together (p. 248).

CHAPTER XVII

CARBON

The Fourth Group

The fourth group contains two non-metals, carbon and silicon, and seven metals.

Sub-Group *a* (Even Series)

	C		Si	Ge	Sn	Pb
Atomic number	6		14	32	50	82
Electron configuration	2·4		2·8·4	2·8·18·4	2·8·18·18·4	2·8·18·32·18·4
	Diam.	Graph.				
Density	3·52	2·25	2·49	5·35	7·3	11·34
Atomic volume	3·4	5·3	11·4	13·6	16·3	18·27
Melting point	3500°		1420°	958·5°	231·84°	327·4°
Boiling point	4200°		2600°	2700°	2260°	1620°

Sub-Group *b* (Odd Series)

	Ti	Zr	Hf	Th
Atomic number	22	40	72	90
Electron configuration	2·8·10·2	2·8·18·10·2	2·8·18·32·10·2	2·8·18·32·18·10·2
Density	4·50	6·53	13·07	11·3
Atomic volume	10·64	14·0	13·66	20·5
Melting point	1800°	1600°	2200°	1845°
Boiling point	> 3000°	> 2900°	3200°	> 3000°

Apart from tin and lead the elements have very high melting points, and all have high boiling points.

The differences between the odd and even series are ill-defined and the electrochemical characters are not very pronounced, the group forming the transition between the electropositive (base-forming) elements of Group III and the electronegative (acid-forming) elements of Group V. The group as a whole occupies the middle of the periods it comprises and hence has a somewhat neutral character, this being particularly marked in the case of carbon, which has only covalency and no electrochemical character.

This neutral character of carbon was the reason why its chemistry was not satisfactorily accommodated by the theory of electrochemical dualism of Berzelius, and led to the replacement of this by " unitary " theories culminating in the old valency theory, which really applied only to covalent compounds.

The division of the Group IV elements into the two series Ge, Sn, Pb and Ti, Zr, Hf, Th is fairly obvious, but the relation of these to the " typical " elements C and Si is far from clear. The increase of electropositive character from Ge to Pb and from Ti to Th, as shown *e.g.* by the capacity for salt formation, is clear, and the heats of formation of the oxides and chlorides increase

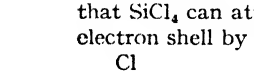
from C to Si, indicating that Si is more electropositive than C. In this respect the *b* or odd series differs from those of earlier groups, in which the electropositive character decreases with increase in atomic weight. Mendeléeff grouped C and Si with Ge, Sn, Pb (as here), whilst Lothar Meyer grouped them with Ti, Zr and Th, with which (*e.g.* in their high m.ps., formation of covalent compounds and their predominating quadrivalency) they show close analogies.

All the elements of Group IV show some amphoteric character, corresponding with their position between the positive elements of Groups I and II and the negative elements of Groups V-VII, and this is probably related to their capacity for forming complex acids, which begins with Si (Abegg, 1909). In the group Ti to Th, Th alone forms definite oxysalts and is the most electropositive element of the whole group.

The elements C, Si, Ge, Sn and (possibly) Pb all form *gaseous hydrides* RH_4 (C and Si also form others, in which the element is always 4-valent), the stability decreasing with increase of atomic weight, so that PbH_4 has only a doubtful existence. The other elements all absorb hydrogen and may form solid hydrides.

The elements all form volatile covalent *tetrachlorides* RCl_4, which except CCl_4 are hydrolysed by water. Tin and lead form lower chlorides $SnCl_2$ and $PbCl_2$ which are very stable.

The abnormal behaviour of CCl_4 has been explained by assuming that water molecules must first add to the central atom by donation of an electron pair of the oxygen in the OH_2 molecule. This is not possible with carbon, since in CCl_4 it is surrounded by 8 electrons, the maximum number possible in the elements of its short period (p. 264). Carbon can neither donate nor accept an electron pair and its behaviour is anomalous. BCl_3, with only 6 electrons, can attach OH_2 making 8, and elements of later periods can have a 12-electron shell, so that $SiCl_4$ can attach $2H_2O$, then forming $4HCl$ and SiO_2. SiF_4 can increase its electron shell by forming SiF_6''. In NCl_3 the nitrogen can act as donor and form



which then forms HOCl (p. 555). SF_6 has already a 12-electron shell and is stable towards water.

C, Si and Ge all form *chloroforms* $RHCl_3$. The b.ps. of the halogen compounds in the two sub-groups are :

CCl_4	76·7°	$CHCl_3$	61·2°	$TiCl_4$	136·4°
$SiCl_4$	56·8°	$SiHCl_3$	31·8°	$ZrCl_4$	sublimes
$GeCl_4$	86·5°	$GeHCl_3$	75·2°	$HfCl_4$	,,
$SnCl_4$	114·1°	—		$ThCl_4$	m.p. 820°, sublimes
$PbCl_4$	decomposes	—			

Silicon is somewhat anomalous. *Oxychlorides* $ROCl_2$ are formed by C, Si, Ge, Zr and Th.

The typical *oxide* is RO_2, stable in the case of all the elements, and on the whole weakly acidic (true peroxides, usually hydrated, are formed only in

sub-group *b*). Lower oxides are also known, and in the case of Sn and Pb the bivalent compounds are generally most stable, the only stable compounds of 4-valent Pb being PbO_2 and some complex compounds. The oxides SnO and PbO are distinctly basic though amphoteric. All the dioxides except CO_2 have high m.ps., but this really depends on the lattice structure (p. 246); only CO_2 forms a molecular lattice of high volatility, whereas silicon shows a great reluctance to form double bonds and SiO_2 is a crystalline solid in which each Si is linked by *single* bonds to *four* oxygens. The high m.ps. of the elements C, Si, Ge, Ti, Zr, Hf and Th are also a result of lattice structure, as they (and also grey tin) form diamond lattices. Bivalent lead shows close analogies with barium, *e.g.* $PbSO_4$ is very sparingly soluble and is isomorphous with $BaSO_4$, with which it often occurs.

Titanium shows valencies of 2, 3 and 4 and is a member of a transitional series: Ti, V, Cr, Mn and Fe (p. 261).

Carbon

Free carbon occurs crystalline as diamond and graphite (both also found in some meteorites) and amorphous as anthracite coal. Combined carbon is ubiquitous; hydrocarbons compose natural gas and petroleum, coal is rich in carbon, carbon dioxide occurs in the atmosphere and carbonates are important minerals, *e.g.* chalk, limestone and marble, $CaCO_3$, magnesite $MgCO_3$, and dolomite $MgCO_3,CaCO_3$. Since carbon atoms can link together to form chains or rings, the number of carbon compounds is very large.

Charcoal or so-called " amorphous carbon " really consists of microcrystals of graphite, and the only true allotropic forms are diamond and graphite.

The heats of combustion at room temperature of 12·01 g. of each are: diamond 94·484 k. cal., graphite 94·030 k. cal., charcoal 96·342 k. cal. (Rossini and Jessop, *J. Res. Bur. Stand.*, 1938, **21**, 457), so that graphite is the stable form at room temperature as well as at high temperatures (p. 441).

Diamond

This gem occurs as rounded " pebbles " in India, Brazil, British Guiana, New South Wales, Arkansas and particularly in British South Africa. Indian and Brazilian diamonds, which are nearly colourless, are the most valuable; South African (Cape) diamonds are often faintly yellow. Most diamonds are small but the Cullinan diamond, discovered at Kimberley in 1905, weighed about $1\frac{1}{8}$ lb. or 3032 carats (1 *carat* = 0·2054 g.; the International carat is 0·200 g.). South African mines supply over 96 p.c. of the world's diamonds.

Transparent diamonds are occasionally blue, pink or green. The cause of the colour is not clear; exposure to cathode rays may deepen the colour, which is lost on heating to 300°–400°, except yellow, which is very stable. The α-rays from radium colour diamond green.

Black or dark-coloured (green, brown, red or grey) diamonds, *carbonado* and *bort* (or *boart*), of no value as gems, are used for rock-drills, lathe tools for

setting abrasive wheels, and when crushed for cutting and polishing clear diamonds.

Boart may mean any impure diamond or even fragments of gem diamonds. *Carbonado* is usually a massive form, granular and without cleavage, or an impure aggregate of small crystals. According to Roth (1925) the heats of combustion of colourless diamond and *carbonado* are 7·873 and 7·884 k. cal. per g. respectively.

The diamond crystallises in the regular or cubic system and forms related to the cube or octahedron, sometimes with curved faces, predominate. By cutting, the natural crystal shape is changed to an artificial form, which gives rise to a large amount of internal reflexion.

Indian diamonds occur in river gravels and alluvial deposits, and are separated by washing. The Kimberley diamonds occur in " blue ground " (usually dark green), which is weathered olivine and runs in large " pipes " through strata of sand, rock, and quartz. Masses of this earth are allowed to weather and crumble to light earth and a small quantity of heavier mineral, which contains the diamonds. The light material is washed off and the heavier residue carried by water over a vibrating greased table, to which only the diamonds adhere. The yield is variable ; in the richest mines it is about 0·1 g. per ton of earth. The origin of diamonds is unknown, but the presence of oxide of iron in diamond-bearing earth and in the ash of diamonds suggests that they may have crystallised from molten iron. The structure of diamond is explained on p. 242. The lattice is redrawn in Fig. 196. Each atom is joined by covalencies to four others surrounding it at the corners of a regular tetrahedron, the distance between the atomic centres being 1·5 A. (Lonsdale, *T. Faraday Soc.*, 1929, **25**, 352). The whole crystal consists of atoms linked by strong covalent bonds, which is said to explain its great hardness, high density and high melting point. An uncommon type of diamond has a laminar structure and unusual properties, including photoelectric conductivity (Robertson, Fox and Martin, *Phil. Trans.*, 1934, **232**, 463).

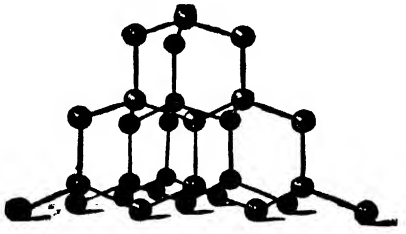


FIG. 196.—Diamond lattice.

The diamond is extremely hard but fairly brittle : it is scratched by no other substance except boron carbide (B_4C) and heads **Mohs' scale of hardness :**

1. Talc. 3. Calcite. 5. Apatite. 7. Quartz. 9. Corundum.
2. Gypsum. 4. Fluorite. 6. Orthoclase. 8. Topaz. 10. Diamond.

Each mineral in the scale is scratched by all below it. In reality, diamond is about 140 times harder than corundum. Drilled diamonds are used as dies for drawing tungsten filaments for electric lamps.

Diamond has a density of 3·51 at 15°, a high refractive index (2·417 for the D-line) and a high dispersive power, giving a play of colours in white light. It is transparent to X-rays whilst imitations are opaque. Many diamonds phosphoresce in cathode rays or ultra-violet light.

Diamond resists almost all chemical reagents: a mixture of potassium dichromate and sulphuric acid oxidises it slowly at 200° to carbon dioxide, and fused sodium carbonate converts it into carbon monoxide. It dissolves in molten iron, and is slowly attacked by sulphur vapour at 1000°. Diamond is stable in vacuum up to 1500°, but at 1800° (more rapidly at 2000°) it forms graphite, the stable variety of carbon at high temperatures and moderate pressure (Lebeau and Picon, *Compt. rend.*, 1924, **179**, 1059).

If heated at 900° in air or 800° in oxygen diamond burns; if pure it leaves only a trace of ash (0·05–0·2 p.c.), chiefly silica and iron oxide; boart may leave as much as 4·5 p.c. of ash and its ignition temperature is higher than that of clear diamond. Diamond burns in oxygen more easily than graphite, and in combustion at a very high temperature (2000°) the clear crystal is covered with a black film, probably of graphite (Moissan, *Ann. Chim.*, 1896, **8**, 466, 478).

Newton in 1704 (*Opticks*, Book II, part 3), arguing from the similarity in refractive indices of diamond and oil of turpentine, camphor, and amber, suggested that it might be "an unctuous [fatty] substance coagulated." The Florentine academicians in 1694–5 had heated a diamond in the focus of a powerful burning glass and found that it glowed red-hot and disappeared. D'Arcet (1766) found that a diamond strongly heated in a *closed* crucible remained unchanged. Allen and Pepys in 1807 burnt diamond in oxygen and showed that it gave the same weight of carbon dioxide as charcoal. Davy in 1814, using the original Florentine lens, burnt a diamond in oxygen. It continued to burn with a steady brilliant light if removed from the focus. Nothing was produced but carbon dioxide. Smithson Tennant (1797) burnt diamonds by strongly heating them in a gold tube with fused nitre (first used for this purpose by Guyton de Morveau in 1785): he found that as much carbon dioxide was formed as Lavoisier (1772) had obtained from an equal weight of charcoal.

Macquer (1771) found that a diamond strongly heated in air burned with a small phosphorescent flame, and Moissan (1896) says diamond burns in oxygen with "a very distinct flame."

EXPT. 1.—The combustion of diamond in oxygen may be shown by electrically heating a splinter of *carbonado* in a spiral of fine platinum wire supported by copper leads in oxygen (Fig. 197). A little lime water afterwards shaken with the gas turns milky.

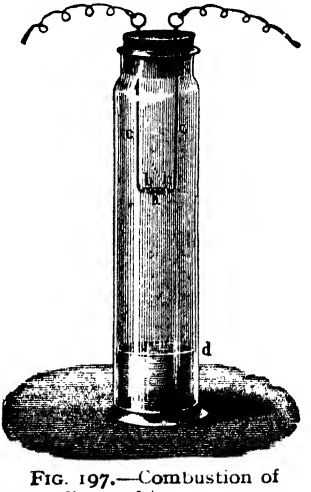


FIG. 197.—Combustion of diamond in oxygen.

Artificial diamonds were made in 1893 by Moissan (*Compt. rend.*, 1893, **116**, 218; *Ann. Chim.*, 1896, **8**, 466). He heated charcoal at a very high temperature with iron in a carbon crucible in an electric arc furnace with carbon rods inside blocks of lime (Fig. 198). Fused iron dissolves carbon; on cooling slowly most of the carbon deposits as scales of graphite. On rapid cooling under ordinary conditions,

the carbon remains in solid solution and white cast-iron is formed. Moissan cooled the iron containing carbon suddenly from 3500° by plunging the crucible into water. On dissolving the iron with hydrochloric acid, a residue was left containing three varieties of carbon: (1) a small amount of graphite, (2) curious brown twisted threads, apparently formed under great pressure, and (3) a portion denser than 3·4 which contained very small diamonds, some black and some transparent, which were isolated by careful purification and analysed by combustion.

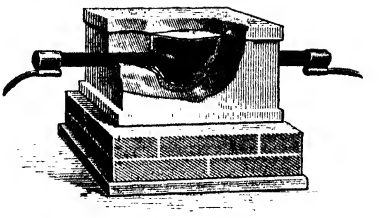


FIG. 198.—Moissan's electric arc-furnace.

Moissan first thought that the enormous pressure developed by the solidification of the molten cast-iron inside the rigid outer skin was necessary, but he afterwards regarded rapid cooling as the essential condition. Moissan's process was successfully repeated by Ruff (*Z. anorg. Chem.*, 1917, **99**, 73), who proved that the crystals were diamonds (and not, *e.g.*, silicon carbide) by several tests.

GRAPHITE

The early mineralogists confused molybdenite (MoS_2) and graphite as *molybdoena* or *black lead*, both being soft grey minerals with a metallic lustre and giving a streak on paper like that made with lead. They were distinguished by Scheele in 1778–9 and the name graphite (Greek *grapho*, I write) was proposed by Werner for plumbago or black lead, a form of carbon. Scheele found that the scales (*kish*) depositing from molten iron in blast furnaces are graphite. Clement and Desormes in 1802 showed that graphite burns in oxygen to give as much carbon dioxide as an equal weight of pure charcoal. It was sometimes thought to be a carbide of iron, as natural graphite leaves a residue of ferric oxide on combustion, but pure artificial graphite free from iron was prepared by Brodie in 1855. Foucault and Fizeau in 1844 obtained graphite by heating charcoal in an electric arc.

Natural graphite occurs mainly in Siberia, Bohemia, Bavaria and Ceylon; the old mines at Borrowdale in Cumberland are worked out. There is some in Canada, California and New York State. Ceylon graphite is purest but Siberian and Bohemian graphites are mostly used for pencils, which go back to the sixteenth century (Mitchell, *J.S.C.I.*, 1919, **38**, 383), when Conrad Gesner describes a pencil made with *stimmi Anglicum* (*i.e.* Borrowdale graphite).

Artificial graphite is made by the Acheson process (1896) at Niagara. A mixture of sand and powdered anthracite or coke (petroleum coke is best) is very strongly heated for twenty-four to thirty hours by an electric current. Carbon rods lead the current through the mass, which is supported on a brick base and covered with sand (Fig. 199).

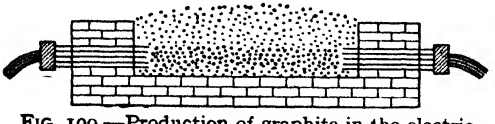


FIG. 199.—Production of graphite in the electric furnace.

The product, which is very pure, soft and free from grit, is used for electrodes, brushes, carbons for dry batteries, and as a lubricant, but not for pencils. With water containing tannin it forms a colloidal suspension used as a lubricant called *deflocculated graphite* or " aquadag " : when kneaded with oil the water is squeezed out and the suspension of graphite in oil is called " oildag " (" dag " = deflocculated Acheson graphite).

Graphite crystallises in grey shining plates belonging to the hexagonal or trigonal system, but is usually found in masses of easily separated thin sheets, which when rubbed flake off in thin layers ; hence it has a greasy feel, makes a streak on paper, and acts as a lubricant. It is used (as " black-lead ") for pencils, and in polishing ironwork and granular gunpowder.

Pure graphite, s. g. 2·25, is a good conductor of heat and electricity, hence graphite is used in cores of arc-carbons, as anodes for electrolytic cells, and for covering moulds on which copper is deposited electrolytically.

Graphite burns only at a high temperature (about 690° in air), and is used for making plumbago crucibles : these consist of 75 parts of plastic clay, 25 of sand, and 100 of graphite, moulded and baked. A granular mixture of graphite, silicon carbide and clay is used as a resistance (*kryptol*) in electric furnaces. Mixed with a little plastic clay and squirted into threads, graphite is used to make black-lead pencils.

Graphite is not attacked by dilute acids or fused alkalis or when heated in chlorine. A mixture of potassium dichromate and sulphuric acid slowly oxidises it to carbon dioxide. It burns brilliantly in fused nitre at a high temperature. It is not attacked by fused sodium sulphate (which dissolves coke and retort carbon) but gives carbon monoxide with fused sodium carbonate. When finely granulated, moistened with fuming nitric acid and heated, some varieties (Siberian and Austrian) do not swell ; others (Ceylon and American) do. This is called *Luzi's test* (1891).

The structure of graphite is shown in Fig. 200. The carbon atoms are arranged in hexagons in flat parallel sheets, each atom being linked to three adjacent atoms at distances of 1·4 A. by strong covalent bonds. The sheets are 3·4 A. apart so that the fourth valency distance is almost too long to constitute a real bond, and there is probably resonance between single and double bonds in the planes. (In the similar boron nitride BN lattice the fourth valency is absent.)

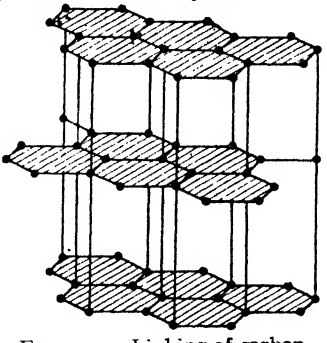


FIG. 200.—Linking of carbon atoms in graphite.

Graphitic oxide.—Charcoal slowly dissolves in hot dilute nitric acid forming a brown substance called " artificial tannin " by Hatchett (1805), and alkaline permanganate oxidises it to oxalic acid and mellitic acid $C_6(COOH)_6$ (a derivative of benzene), the aluminium salt of which occurs as the mineral honey-stone.

Graphite is oxidised by a mixture of concentrated sulphuric and nitric acids and some potassium chlorate to a peculiar solid called **graphitic acid** by its dis-

coverer Brodie (1859), and **graphitic oxide** by Berthelot (1869). Its formation has been regarded as a test for graphite, but small amounts have been obtained from some kinds of so-called amorphous carbon (Hofmann and Frenzel, *Ber.*, 1930, **63**, 1248; Riley, *J.S.C.I.*, 1939, **58**, 391).

One g. of powdered pure Ceylon graphite is added to a cooled mixture of 40 c.c. of conc. H_2SO_4 and 20 c.c. of 60 p.c. HNO_3. To the mixture are added in small portions over a period of 1½ hours 20 g. of $KClO_3$, with shaking. The mixture is allowed to stand 16 hours and then poured into 1 lit. of distilled water. The graphitic oxide is washed by decantation till free from acid, filtered (it is difficult to filter) and dried in a desiccator over P_2O_5, when it forms a mass like varnish (Hofmann, *Ber.*, 1928, **61**, 435).

Graphitic oxide is microcrystalline or amorphous in appearance, but the X-rays show that it is crystalline (Hofmann, *loc. cit.*). The crude greenish product becomes bright yellow when moist after purification by treatment with *acid* permanganate (Berthelot), but is brown when dry. It is almost insoluble in water but reddens moist litmus paper.

There has been much discussion of the formula of graphitic acid or graphitic oxide. Brodie found $C_{11}H_4O_5$ ($C_{11}O_3,2H_2O$); Hulett and Nelson (1920) suggested C_3O or $C_{11}O_4$; Hofmann, etc. (*Annalen*, 1934, **510**, 1; *Ber.*, 1939, **72**, 754) find the ratio C : O varies from 4 : 1 to 2 : 1, and since graphitic oxide can be methylated it contains combined oxygen, perhaps attached by ethylene oxide links  to carbon atoms in a graphite lattice.

On heating to about 200° graphitic oxide decomposes suddenly and violently with incandescence, giving a voluminous black powder which Berthelot called *pyrographitic oxide* and Brodie formulated as $C_{22}H_2O_4$ ($C_{22}O_3,H_2O$); it may be graphite. By heating with fuming hydriodic acid in a sealed tube, Berthelot converted graphitic oxide into *hydrographitic oxide*, which does not give pyrographitic oxide on heating.

A mixture of potassium chlorate and concentrated sulphuric acid converts graphite into a black substance containing hydrogen, oxygen and sulphuric acid, called *graphon sulphate* by Brodie. On heating, this swells up, evolves gas, and gives a fine powder of graphite. If this is thrown on water, the impurities sink and the pure graphite (s. g. 2·25) remains floating.

Other *graphite salts* with nitric, perchloric and pyrophosphoric acids have been prepared (Hofmann, etc., *Z. anorg. Chem.*, 1938, **238**, 1). They are coloured and the acid radicals (HSO_4', NO_3', P_2O_7'''', etc.) seem to be contained in the spacings between the sheets of carbon atoms in the graphite lattice.

Charcoal

Besides crystalline diamond and graphite many kinds of black so-called "amorphous carbon" are recognised, all of which may be collectively called *charcoal*. Their different properties seem to depend mainly on the different surfaces (including internal pores) exposed by the same mass. They are all black and opaque, the hardness and density depending largely on the tempera-

ture at which they were formed. The X-ray spectra show that they all contain microcrystalline material with the same arrangement of atoms as in graphite, the crystallites, or small units of the graphite lattice, being in random orientation, so producing what is called a *mesomorphic* state.

The crystallites may be very small (Warren, *J. Chem. Phys.*, 1934, **2**, 551 ; Riley, *J.S.C.I.*, 1939, **58**, 391) ; it is estimated that the finest carbon black consists of particles of size 60 A. by 10 A. containing two or three layers of about 400 graphite rings in each. The actual particles in a fine carbon black such as is used as a rubber " filler " are 0·1–0·2μ diam.

The various forms of charcoal (Mantell, *Industrial Carbon*, 1928) are usually classified as :

1. *Charcoal* from wood, cellulose, sugar, etc.
2. *Lampblack* from the smoke of burning oils, fats, resins, etc. ; *carbon black* made by burning natural gas (CH_4) and depositing the soot on cooled metal plates ; *acetylene black*, from the explosive decomposition of acetylene (99·6 p.c. C). All these are used as pigments and as " fillers " for rubber, greatly increasing its tensile strength.
3. *Animal charcoal* (*bone-charcoal, ivory black*) made by charring bones and used for decolorising sugar syrup, etc.
4. *Gas carbon*, deposited on the wall of the retort in making coal gas.
5. *Coke*.
6. *Electrode carbon* made by heating a mixture of anthracite, petroleum coke, etc., with a binder such as pitch, at a temperature below that at which graphitising occurs.

The purest *charcoal* is made by heating pure cane sugar in a large covered crucible till no more gas is evolved, heating the charcoal for some hours at 1000° in a graphite tube in a current of chlorine to remove residual *combined* hydrogen as HCl, washing, and igniting in hydrogen to remove chlorine (Bone and Jerdan, *J.C.S.*, 1897, **71**, 41) : charcoal adsorbs very little free hydrogen. Charcoal so prepared has a density of 1·57 to 1·8 and ignites in air at 450°. Pure amorphous carbon free from hydrogen is also formed, mixed with magnesia, by burning magnesium in carbon dioxide.

The low ignition temperature of charcoal as compared with other forms of carbon is seen from Moissan's results in oxygen :

	Diamond	Graphite	Wood charcoal
Evolution of CO_2 begins - -	720°	570°	200°
,, ,, ,, abundant -	790°	600°	—
Burns with flame - - -	800°–850°	690°	345°

Wood charcoal is made by charring wood either in a heap (*meiler*) covered with turf, or in a closed oven or retort. It contains about 93 p.c. of carbon, 2·5 p.c. of hydrogen and 3 p.c. of ash (chiefly calcium and potassium carbonates). By heating above 1500° the hydrogen falls to 0·62 p.c. The yield in meilers is about 24 p.c. of the wood, in ovens about 25 p.c. with 10 p.c. of tar, 40 p.c. of " pyroligneous acid " (= 2 p.c. of glacial acetic acid) and 25 p.c. of gas.

Active charcoal, used as an adsorbent, is made from suitable charcoal, peat, or coal by different methods.

In the *direct process* the charcoal, or low-temperature coke from suitable coal, is heated in retorts at 1000° in presence of a regulated amount of air or steam, which removes material obstructing the pores. In the *briquetting process* (now mostly used) the powdered charcoal (*e.g.* beechwood charcoal for the variety called *norit*) is agglomerated with wood tar and a little caustic soda and the granules subjected to progressive heating, finally in steam at 800°–1000°. In the *chemical process* wood or peat is mixed with salts such as magnesium or zinc chloride, or with phosphoric acid, and carbonised, after which the soluble material is removed from the charcoal by washing with dilute acid.

Active charcoal adsorbs more gas than ordinary charcoal (p. 89) and is used in respirators; it is also used, as well as animal charcoal and blood charcoal, for decolorising sugar syrup (Derosne, 1812), and for removing fusel oil from crude spirit. It is "revivified" by boiling with caustic soda solution and washing, animal charcoal by heating in retorts.

Wood charcoal is a black friable material retaining more or less the original shape of the wood but diminished in volume. Although the true s. g. of air-free charcoal is 1·3 to 1·9, the mass is very porous, has an apparent s. g. of 0·2 to 0·5, and floats on water. If the air is removed by an air pump, the charcoal gives out bubbles and slowly sinks. Charcoal is very permanent on exposure to air and moisture.

Gas carbon is a pure greyish-black hard form of carbon, s. g. 2·35, and a good conductor of electricity, which is deposited by the decomposition of methane in contact with the red-hot wall of the retort in making coal gas (p. 451).

According to Hofmann and Röchling (*Ber.*, 1923, **56**, 2071) it is a mixture of graphite with a very hard *lustrous carbon*, silvery in appearance, s. g. 2·07, a moderately good conductor of electricity and deposited in a brilliant layer on a glazed porcelain surface at 800°–1000° from gas containing methane. It is chemically very indifferent, resisting nitric acid and even fused sodium sulphate.

Coal is a mineral rich in carbon which is the final result of a series of decompositions in presence of a limited supply of air, high pressure and perhaps heat, undergone by vegetable matter in the remote past. Some carbon, hydrogen and oxygen were eliminated as carbon dioxide, water and methane, and the residue became increasingly richer in carbon. Bituminous coal contains hardly any free carbon and a large fraction (up to 40 p.c.) is soluble in pyridine. On oxidation with permanganate it gives acids of the aromatic series, and it always contains sulphur and nitrogen as organic compounds (Bone and Himus, *Coal: its Constitution and Uses*, 1936).

The successive stages in the conversion of vegetable matter into coal are supposed to be: *peat*, *lignite* (or *brown coal*), *true coal*, and *anthracite*. Some think graphite is the final stage.

Stopes (1919), from microscopic investigations, recognised four constituents in banded coal, which she named *durain*, *fusain*, *vitrain* and *clarain*. Their

behaviour on coking (heating out of contact with air) is different (Lessing, *J.C.S.*, 1920, **117**, 247). Fusain gives a powdery coke, and durain coke is also very friable; with clarain fusion and swelling occur and a coherent brown coke is formed; vitrain also fuses but gives a silver-white coke with excrescences. The four constituents also show different adsorptive capacities for pyridine vapour. Vitrain and clarain are bright, durain is dull, and fusain is dull and friable like charcoal.

Common or *bituminous coals*, which burn with a bright smoky flame, are divided into *caking* and *non-caking* according as they do or do not soften and fuse together on burning or coking. *Cannel coal* (with the Scotch variety *torbanite* or *Boghead coal*) is compact, dull grey or black, non-lustrous, breaking with a conchoidal fracture and yielding a large amount of gas and only a little coke of inferior quality. *Jet*, found at Whitby, is a hard lustrous variety of cannel coal. The last stage in coal formation, very rich in carbon, is *anthracite*, with a high ignition point, usually a brilliant lustre and a conchoidal fracture. It burns without flame. It occurs locally in many coalfields, such as South Wales, Scotland, and Pennsylvania.

The table shows the change in composition during the conversion of woody matter into coal (the nitrogen and sulphur are neglected), with corresponding increase in calorific value.

	Carbon	Hydrogen	Oxygen	Calorific Value B.Th.U. per lb.
Wood	50·0	6·0	44·0	7,400
Peat	60·0	5·9	34·1	9,900
Lignite	67·0	5·2	27·8	11,700
Bituminous coal	88·4	5·6	6·0	14,950
Welsh steam coal	92·5	4·7	2·7	15,720
Anthracite	94·1	3·4	2·5	15,720
Pure charcoal	100·0	—	—	14,544
Petroleum	85·5	14·2	0·3	19,800
Methylated spirit	52·2	13·0	34·8	11,160
Coal gas	—	—	—	19,220
Hydrogen	—	100·0	—	62,100

(A British Thermal Unit raises 1 lb. of water 1° F.; 1 k. cal. = 3·968 B.Th.U. The values for wood, peat, etc., refer to materials free from moisture: the actual materials contain water and the calorific values are smaller. The values for pure charcoal, coal gas, hydrogen, methylated spirit, and petroleum are given for comparison.)

Coal is converted into oil by *hydrogenation*. A mixture of powdered cleaned coal made into a paste with an equal weight of hydrocarbon oil is treated with hydrogen gas at 450° at 250 atm. pressure. The coal is mostly transformed into oil, which is vaporised and separated by fractionation into gasoline, middle oil and heavy oil, the last being rehydrogenated to gasoline and middle oil. The middle oil is hydrogenated in the vapour form in presence of a solid catalyst. The small solid residue of the coal can be used as fuel. Creosote oil and low temperature tars (p. 460) can also be hydrogenated.

The **calorific value** of a fuel is expressed in thermal units evolved by the complete combustion of unit mass of fuel, the water formed being supposed condensed to liquid. It is determined by burning a weighed amount of the solid or liquid fuel in compressed oxygen in a strong metal **bomb calorimeter** (Fig. 201). Ignition is by a known weight of iron wire heated by an electric current and supported over a platinum spoon containing the fuel. The bomb is immersed in water in a calorimeter. The heat of combustion of the iron wire is subtracted from the total heat evolved.

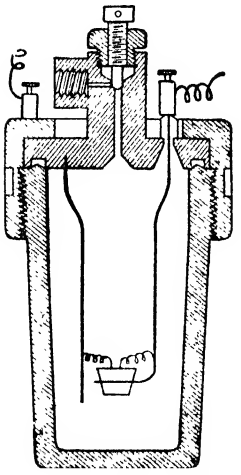


FIG. 201.—Bomb calorimeter.

CARBIDES

Compounds of metals with carbon, the *carbides*, are of two main types :

(i) **Refractory carbides** (of Ti, Zr, Hf, V, Nb, Ta, Mo and W), of very high m.ps., metallic conductors (also supra-conductors, *i.e.* having a very large conductivity at very low temperatures), weakly paramagnetic and not attacked by water or acids. They are *interstitial compounds* (Westgren, *J. Franklin Inst.*, 1931, **212**, 577), with small carbon atoms inserted into the spaces of the slightly expanded metal lattice. The lattices of TiC, VC, ZrC, NbC and TaC are of the rock-salt type (Fig. 144), although made up of neutral atoms. Other types are Mo_2C and W_2C, tungsten carbide being very hard and used for cutting and grinding very hard materials. Tantalum carbide with a cobalt binder is much harder even than tungsten carbide, and although expensive has been used for tools.

When the non-metal atoms are decidedly smaller than the metal atoms, the lattice is a face- or body-centred cubic, or a close-packed hexagonal, or a simple hexagonal, sometimes slightly distorted, the non-metal atoms filling the voids in the metal lattice. When the atomic ratio exceeds 0·59 the voids are not large enough and more complicated structures result.

(ii) **Salt-like carbides** with ionic lattices, with metal cations in the interstices between carbon anions. With large cations the carbon lattice is deformed and breaks up into separate anions, either C_2^{--} giving acetylene with water (*e.g.* in CaC_2), or $C^{==}$ giving methane (in Be_2C and Al_4C_3).

In Fe_3C, which is isomorphous with Mn_3C and $(Mn, Fe)_3C$ (*spiegeleisen*), the carbon atoms are inside a trigonal prism. Chromium carbide Cr_3C_2 is a special type, neither salt-like nor interstitial, the carbon atoms being linked in zig-zag chains of a paraffin hydrocarbon skeleton spreading through the metal lattice (Westgren, 1932–3).

When the carbon atoms occur in pairs as C_2^{--} ions the metal lattice is deformed along one axis and the direction of the —C≡C— axis varies ; the structures proposed for CaC_2 and ThC_2 are shown in Fig. 202 (Stackelberg, *Z. phys. Chem.*, 1930, **9B**, 437 ; 1934, **27B**, 53 ; cf. Hägg, *ibid.*, 1929, **6B**, 221 ; 1931, **12B**, 33)

In *Group I* only lithium combines directly with carbon forming Li_2C_2, but all the alkali metals form carbides Me_2C_2 on heating in acetylene. They give acetylene with water and probably contain $[—C{\equiv}C—]''$ ions. Copper (cuprous),

silver and gold (aurous) carbides Me_2C_2 are also acetylides, and are precipitated by acetylene from ammoniacal cuprous and silver solutions and sodium gold thiosulphate solution. They are explosive.

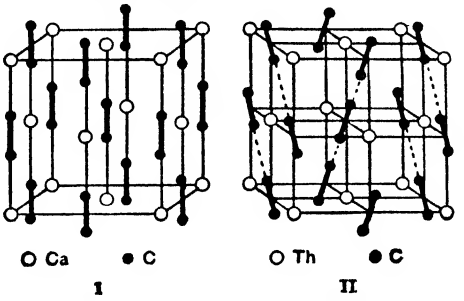


FIG. 202.—Structure of carbides.

In *Group II* beryllium and calcium form carbides Be_2C and CaC_2 directly ; these and SrC_2 and BaC_2 are formed from the oxides and carbon in the electric furnace. Beryllium carbide with water gives methane : $Be_2C + 2H_2O = 2BeO + CH_4$, the others give acetylene : $CaC_2 + 2H_2O = Ca(OH)_2 + C_2H_2$. Traces of the magnesium carbides Mg_2C (giving acetylene with water) and Mg_2C_3 (giving allylene $CH_3{\cdot}C \vdots H$ with water) are formed from the elements. Zinc carbide ZnC_2 is formed from acetylene and zinc ethyl, cadmium carbide CdC_2 from acetylene and a compound of cadmium iodide and aniline ; mercurous carbide Hg_2C_2,H_2O is precipitated by acetylene from a suspension of mercurous acetate, and mercuric carbide $3HgC_2,H_2O$ by acetylene from a solution of mercuric oxide in ammonia and ammonium carbonate.

In *Group III* aluminium forms Al_4C_3 directly ; it evolves methane with water : $Al_4C_3 + 12H_2O = 4Al(OH)_3 + 3CH_4$. The rare earth carbides MeC_2 (except Ce_2C_6 in addition to CeC_2), formed from the oxides and carbon in the electric furnace, give with water and acids a mixture of hydrocarbons, including acetylene and ethylene, and free hydrogen.

In *Group IV* (besides silicon carbide SiC) refractory carbides are formed by heating titanium, zirconium and hafnium oxides with carbon in the electric furnace. The compound $HfC,4TaC$ has the very high m.p. 3942°. Thorium carbide ThC_2, from the oxide and carbon in the electric furnace, is decomposed by water into a mixture of hydrocarbons. Germanium, tin and lead form no definite carbides.

In *Group V* hard and refractory carbides V_2C, VC, VC_2, NbC and TaC are formed in the electric furnace. Ill-defined phosphorus and arsenic carbides, PC_3 and AsC_3, have been described, but no antimony or bismuth carbides are known.

In *Group VI* Cr_3C_2, Cr_5C_2, Mo_2C, MoC, W_2C and WC are refractory carbides. Uranium carbide UC_2, formed in the electric furnace from UO_2 and carbon, is very hard but easily oxidises and is decomposed by water like the rare earth carbides. CS_2 and CSe_2 are known but no tellurium carbide.

In *Group VII* manganese carbide Mn_3C, formed in the electric furnace, appears metallic but easily oxidises in moist air and decomposes water : $Mn_3C + 6H_2O = 3Mn(OH)_2 + CH_4 + H_2$. Other carbides reported are MnC_2, $Mn_{23}C_6$ and Mn_7C_3. Highly active rhenium in carbon monoxide at 470°–600° forms a carbide, but this is completely decomposed at 1600°.

In *Group VIII* iron carbide Fe_3C (*cementite*) remains after the action of fuming nitric acid on steel borings; it dissolves in concentrated hydrochloric acid with evolution of a mixture of hydrocarbons. Cobalt and nickel carbides are not known, but $(Fe,Co,Ni)_3C$ is *cohenite*, found in some meteorites. No platinum metal carbides are known.

Hydrocarbons

Methane CH_4 is formed by the bacterial decay of vegetation (cellulose) at the bottom of marshy pools: $C_6H_{10}O_5 + H_2O = 3CH_4 + 3CO_2$, and the *marsh gas* liberated in bubbles consists mainly of methane (which was discovered in it by Volta in 1776) and carbon dioxide. Methane is also occluded in coal and escapes when the pressure is relieved, forming *fire-damp*, which when mixed with air causes explosions when kindled. The gas often issues in large quantities from "blowers" or fissures in the coal and contains 80–98 p.c. of methane, with some ethane (C_2H_6), carbon dioxide and nitrogen (Dixon and Bone, *Proc. C.S.*, 1903, **19**, 63): the nitrogen contains twice as much helium as atmospheric nitrogen. *Natural gas* from petroleum wells contains more than 90 p.c. of methane and the gas from some kinds of rock salt is rich in methane.

Methane is formed by direct combination of carbon and hydrogen at high temperatures: $C + 2H_2 \rightleftharpoons CH_4$.

By circulating hydrogen over heated sugar-charcoal more than 95 p.c. of the theoretical yield is produced. Between 1100° and 2100° at pressures up to 200 atm. methane is the only saturated hydrocarbon formed: ethylene and acetylene are formed in smaller amounts. The percentages of methane in equilibrium with carbon and hydrogen at atmospheric pressure are: 850°, 2·5; 1000°, 1·1; 1100°, 0·6 (Bone and Coward, *J.C.S.*, 1908, **93**, 1975; 1910, **97**, 1219; Coward and Wilson, *ibid.*, 1919, **115**, 1380; Pring and Fairlie, *ibid.*, 1911, **99**, 1796). Methane is formed when a mixture of hydrogen and carbon monoxide is passed over reduced nickel at 250° to 400°: $CO + 3H_2 = CH_4 + H_2O$.

Methane is usually prepared in the laboratory by heating a mixture of anhydrous sodium acetate with three times its weight of soda-lime in a hard glass or copper flask:

$$CH_3{\cdot}COONa + NaOH = Na_2CO_3 + CH_4,$$

or a mixture of crystalline sodium acetate with 3 to 4 times its weight of barium oxide (Dumas, 1840):

$$2CH_3COONa + H_2O + BaO = Na_2CO_3 + BaCO_3 + 2CH_4.$$

It may be collected over water. Prepared in this way it may contain up to 8 p.c. of hydrogen and 10 p.c. of unsaturated hydrocarbons such as ethylene, which cause it to burn with a slightly luminous flame (Wheeler, *J.C.S.*, 1914, **105**, 2606).

Pure methane is prepared by the action of water on zinc methyl (Frankland, 1852; Campbell and Parker, *J.C.S.*, 1913, **103**, 1292):

$$Zn(CH_3)_2 + 2H_2O = Zn(OH)_2 + 2CH_4,$$

or by the action of copper-zinc couple (Gladstone and Tribe, *J.C.S.*, 1884, **45**,

154) or amalgamated aluminium (Bone and Wheeler, *J.C.S.*, 1902, **81**, 535) on a mixture of methyl iodide and methyl alcohol:

$$CH_3I + CH_3OH + Zn = ZnI(OCH_3) + CH_4,$$
$$3CH_3I + 3CH_3OH + 2Al = Al(OCH_3)_3 + AlI_3 + 3CH_4.$$

Small pieces of aluminium sheet are amalgamated by immersing in mercuric chloride solution, washed with dry methyl alcohol, covered with methyl iodide, and cooled in ice. The mixture of methyl iodide and methyl alcohol is dropped on from a tap-funnel.

Fairly pure methane from the action of water on aluminium carbide: $Al_4C_3 + 12H_2O = 4Al(OH)_3 + 3CH_4$, is purified from hydrogen by adding a little more pure oxygen than is necessary to combine with the hydrogen, passing over palladium black or palladium asbestos at 100°, and removing the excess of oxygen by pyrogallol solution (Campbell and Parker, 1913).

Pure methane is a colourless, odourless, non-poisonous gas, normal density 0·7168 g./lit., b.p. −161·4°, m.p. −185·8°, critical temperature −82·85° and critical pressure 45·6 atm. It is sparingly soluble in water (5·56 vols. in 100 vols. at 0°, 3·3 vols. at 20°), and is somewhat more soluble in alcohol.

Methane is very stable and decomposes only on prolonged sparking (Buff and Hofmann, *J.C.S.*, 1860, **12**, 273) or when strongly heated, reaction taking place on the surface of the vessel with deposition of a dense form of carbon. The decomposition is inappreciable at 700°, and sixty times faster at 985° than at 785°. Other hydrocarbons (ethane, ethylene, etc.) are decomposed in the gas phase at 800° and some acetylene is also formed (Bone and Wheeler, *J.C.S.*, 1902, **81**, 535; Bone and Coward, *J.C.S.*, 1908, **93**, 1975; 1910, **97**, 1219). Methane burns in air or oxygen with a pale, slightly luminous flame: $CH_4 + 2O_2 = CO_2 + 2H_2O$; its ignition point in air is high, 650°–750°. When mixed with oxygen or air it forms a violently explosive mixture: 1 vol. requires 2 vols. of oxygen or 9·5 vols. of air for complete combustion.

By the slow combustion of a mixture of methane with air or oxygen passed over heated porcelain, traces of formaldehyde are formed: $CH_4 + O_2 = H{\cdot}COH + H_2O$. A mixture of 1 vol. of methane and 2 vols. of chlorine burns with a dull flame when kindled, forming fumes of hydrogen chloride and a black cloud of carbon: $CH_4 + 2Cl_2 = C + 4HCl$. A mixture of methane and chlorine slowly reacts in diffused daylight forming substitution products: CH_3Cl (methyl chloride), CH_2Cl_2 (methylene chloride), $CHCl_3$ (chloroform) and CCl_4 (carbon tetrachloride), *e.g.* $CH_4 + Cl_2 = CH_3Cl + HCl$ (Pfeifer, etc., *J.C.S.*, 1919, **116**, i, 565). Since methane reacts only by substitution or decomposition, not by addition, it is called a *saturated hydrocarbon*.

Ethylene.—Although obscurely mentioned by Becher in 1669, the preparation of ethylene C_2H_4 was first clearly described in 1795 by the associated Dutch chemists Deimann, Bondt, Lauwerenburgh and Troostwijk. It was called *olefiant gas* by Fourcroy since it forms an oily compound ($C_2H_4Cl_2$) with chlorine; it was also called *heavy carburetted hydrogen*, and was clearly distinguished from *light carburetted hydrogen* (methane) by Dalton and by Henry in 1805.

Traces of ethylene are formed in the synthesis of methane from carbon and hydrogen at high temperatures and may be adsorbed by passing the cooled gas over charcoal cooled in liquid air. Most of the ethylene decomposes; at 1200° the ratio of methane to ethylene is 100 : 1, at 1400° it is 10 : 1.

Ethylene is formed by passing alcohol vapour over thorium dioxide or alumina (which act as catalysts) at 340°–350°: $C_2H_5OH = C_2H_4 + H_2O$, and by heating alcohol with zinc chloride, boron trioxide, phosphorus pentoxide, concentrated sulphuric acid, or syrupy phosphoric acid. With sulphuric acid, ethylsulphuric acid is first formed and then decomposes:

$$C_2H_5OH + H_2SO_4 = C_2H_5HSO_4 + H_2O,$$
$$C_2H_5HSO_4 = C_2H_4 + H_2SO_4.$$

EXPT. 2.—30 c.c. of alcohol and 80 c.c. of concentrated sulphuric acid are heated in a litre flask at 160°–170°, and a mixture of equal volumes of alcohol and sulphuric acid dropped in from a tap-funnel. To minimise frothing 25 g. of alum may be put in the flask. The gas is washed with water and caustic soda solution to remove carbon dioxide and sulphur dioxide and is collected over water (Fig. 203). It is difficult to prepare pure ethylene by this method.

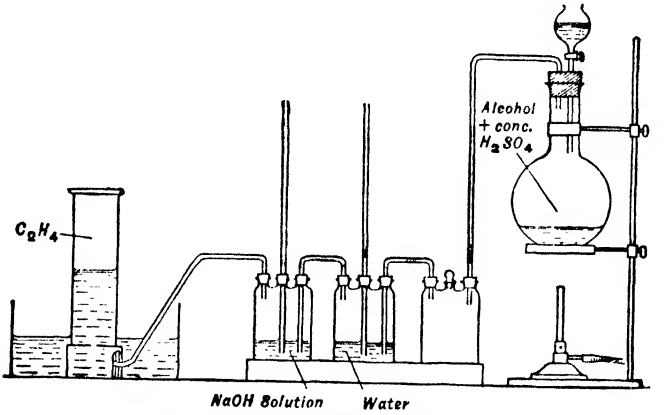


FIG. 203.—Preparation of ethylene.

EXPT. 3.—In Newth's method (*J.C.S.*, 1901, **79**, 915) alcohol is dropped by a tube reaching to the bottom of a distilling flask into 50 c.c. of syrupy phosphoric acid which has been boiled till the temperature rises to 200°–220°; or alcohol vapour from one flask is passed through the phosphoric acid at 220° in a second flask. The gas is passed through a tube cooled in ice and collected over saturated sodium sulphate solution. It is pure.

Ethylene is a colourless gas with a sweet smell, b.p. −103·7°, m.p. −169·5°, critical temperature 9·5°, critical pressure 50·65 atm. It has been used as an anaesthetic and for "ripening" fruit. It is slightly soluble in water (0·163 in 1 vol. at 18°) and more soluble in alcohol (2·75 vols. in 1 vol. at 18°). On sparking it decomposes into carbon and hydrogen, and when passed through a

red-hot tube it gives hydrogen, methane and acetylene, and deposits a brilliant film of carbon.

The thermal decomposition of ethylene is supposed (Bone and Coward, *J.C.S.*, 1908, **93**, 1197; Rice, etc., *J.A.C.S.*, 1932, **54**, 3529) to involve the free radical HC≡≡ as follows:

$$H_2C{:}CH_2 \rightarrow 2CH\,\vdots + H_2 \begin{cases} \nearrow (a)\ C_2H_2 + H_2. \\ \rightarrow (b)\ 2C + H_2 + H_2. \\ \searrow (c)\ C_2H_2 + 3H_2 = 2CH_4. \end{cases}$$

Ethylene burns in air with a smoky luminous flame; in oxygen the flame is very bright and does not smoke. When mixed with 3 vols. of oxygen and kindled it explodes *very violently*: $C_2H_4 + 3O_2 = 2CO_2 + 2H_2O$. When a mixture with an equal volume of oxygen is fired by a spark, expansion occurs and carbon monoxide and hydrogen are formed: $C_2H_4 + O_2 = 2CO + 2H_2$. If the resulting mixture, which burns with a blue flame in air, is mixed with half its bulk of oxygen and again exploded, carbon dioxide and steam are formed: $2CO + 2H_2 + 2O_2 = 2CO_2 + 2H_2O$ (Clement and Desormes, 1801; Dalton, 1810).

When ethylene is mixed over water with an equal volume of chlorine and the mixture exposed to light contraction occurs and oily drops of **ethylene dichloride** ("Dutch liquid") $C_2H_4Cl_2$ collect on the surface of the water:

$$H_2C{:}CH_2 + Cl_2 = CH_2Cl{\cdot}CH_2Cl.$$

Since ethylene forms direct addition compounds it is called an *unsaturated hydrocarbon*. If passed into bromine covered with a layer of water, ethylene forms a colourless pleasant-smelling liquid, **ethylene dibromide** $C_2H_4Br_2$ or $CH_2Br{\cdot}CH_2Br$, similar to the dichloride.

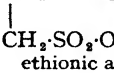
The reaction between dry ethylene and bromine vapour is catalysed by the surface of the glass vessel, and does not take place if this is covered with paraffin wax (Norrish, *J.C.S.*, 1923, **123**, 3006).

A mixture of 1 vol. of ethylene and 2 vols. of chlorine when kindled burns with a red flame, fumes of hydrochloric acid and a dense black cloud of soot being formed: $C_2H_4 + 2Cl_2 = 4HCl + 2C$.

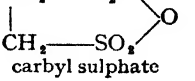
Concentrated sulphuric acid absorbs ethylene slowly on shaking at the ordinary temperature (Faraday, *Phil. Trans.*, 1825, **115**, 440) and rapidly at 160°–170°, with the formation of **ethylsulphuric acid** or **sulphovinic acid** $C_2H_5{\cdot}HSO_4$: $C_2H_4 + H{\cdot}HSO_4 = C_2H_5{\cdot}HSO_4$ (Hennell, *Phil. Trans.*, 1826, **116**, 240). When this is boiled with water, alcohol is produced:

$$C_2H_5{\cdot}HSO_4 + HOH = C_2H_5{\cdot}OH + H_2SO_4$$

(Hennell, *Phil. Trans.*, 1828, **118**, 365). Fuming sulphuric acid rapidly absorbs ethylene forming **ethionic acid** $C_2H_4{\cdot}H_2S_2O_7$ and **carbyl sulphate** $C_2H_4{\cdot}S_2O_6$:



ethionic acid



carbyl sulphate

Acetylene.—By the action of water on potassium carbide formed in the preparation of the metal from potassium carbonate and charcoal, Edmund Davy (1836) obtained a hydrocarbon (called *klumene*), which was rediscovered by Berthelot (*Compt. rend.*, 1860, **50**, 805) and called acetylene. He showed that it is formed on passing ethylene or alcohol vapour through a red-hot tube, and by direct synthesis from its elements when an electric arc burns between carbon poles in an atmosphere of hydrogen (*Compt. rend.*, 1862, **54**, 640) (Fig. 204): $2C + H_2 \rightleftharpoons C_2H_2$. Small quantities of methane and ethane are also

FIG. 204.—Berthelot's synthesis of acetylene.

formed, apparently by independent reactions (Bone and Jerdan, *J.C.S.*, 1901, **79**, 1042).

Acetylene is formed when a Bunsen burner " strikes back " and the gas burns at the inner jet, the flame being cooled by the metal tube (Reith, 1867), and may be formed by the thermal decomposition of the ethylene in the coal gas. The peculiar smell noticed seems to be due to some other substance, perhaps formaldehyde.

EXPT. 4.—The acetylene in the gas is detected by holding over the burner a globe wetted inside with ammoniacal cuprous chloride solution. The dark blue liquid rapidly becomes covered with a red film of cuprous acetylide, Cu_2C_2. By aspirating the gas through the solution in a wash bottle a red precipitate of Cu_2C_2 is formed (*which is explosive when dry*), and by filtering, washing, and warming this with concentrated hydrochloric acid or potassium cyanide solution, pure acetylene is evolved: $Cu_2C_2 + 2KCN + 2H_2O = 2CuCN + 2KOH + C_2H_2$.

Acetylene is prepared by the action of water on calcium carbide (Wöhler, 1862): $CaC_2 + 2H_2O = Ca(OH)_2 + C_2H_2$.

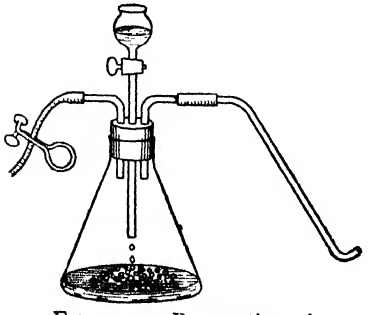


FIG. 205.—Preparation of acetylene.

EXPT. 5.—Cover the bottom of a flask with a layer of sand and place on this a small heap of calcium carbide (Fig. 205). Displace the air with coal gas and allow water to drop slowly on the carbide. Acetylene is rapidly evolved and will burn with a very luminous, smoky flame. The acetylene from commercial carbide has an unpleasant smell, due to impurities such as phosphine, which are removed by passing through a solution of bleaching powder or through a tube loosely packed with slaked lime (cf. Kistiakowsky and Smith, *J.A.C.S.*, 1939, **61**, 1868).

Acetylene is a colourless gas with an ethereal smell when pure. It is non-poisonous in small quantities and can be used as an anaesthetic. Acetylene forms with haemoglobin a compound which, unlike that formed by carbon monoxide, is unstable and readily decomposed by aeration. When strongly cooled acetylene forms a white solid subliming at $-83{\cdot}6°$. Under 1·25 atm. pressure the solid melts at $-81°$ to a colourless liquid. The critical temperature is 35·5°, the critical pressure 61·65 atm. The gas dissolves in its own volume of water at 15° and is more soluble in alcohol.

Acetylene ignites at 428° in air. If the gas is supplied to special burners under a pressure of 2–8 in. of water, so as to escape through fine capillaries and mix with a regulated amount of air, the flame is very bright and does not smoke. Mixtures with air containing the wide range of 2·6 to 80 p.c. of acetylene by volume are explosive, and mixtures of acetylene and oxygen detonate with *extreme violence*, even quite strong glass vessels being shattered by the explosion: $2C_2H_2 + 5O_2 = 4CO_2 + 2H_2O$.

Coal gas is explosive only when mixed with air within the limits 1 of gas to 5–13 of air, and the lower limit of explosion for methane is 5·4 p.c. in air. The danger of explosion with acetylene is, therefore, much greater than with coal gas (Burrell and Robertson, *Ind. Eng. Chem.*, 1911, **7**, 417; Coward, *Bull.* (*U.S.*) *Bur. Mines*, 1931, 279).

Acetylene is strongly endothermic: $2C + H_2 = C_2H_2 - 47{\cdot}8$ k. cal., is unstable, and readily explodes under moderate pressure. It is therefore generated only as required or is absorbed in acetone, which dissolves 300 vols. of the gas under 12 atm. pressure (p. 286).

Chlorine explodes *violently* with acetylene, but by passing the gases alternately into sulphur chloride containing a little reduced iron, combination occurs to the dichloride CHCl:CHCl and the tetrachloride $CHCl_2{\cdot}CHCl_2$. These are used as solvents.

Acetylene is easily converted into acetaldehyde: $C_2H_2 + H_2O = CH_3{\cdot}CHO$ by passing into hot diluted sulphuric acid containing a little mercuric sulphate (Chapman and Jenkins, *J.C.S.*, 1919, **115**, 847; 1921, **119**, 747).

On heating to dull redness, acetylene polymerises into a liquid mixture of hydrocarbons containing benzene (Berthelot, *Ann. Chim.*, 1866, **9**, 445): $3C_2H_2 = C_6H_6$. A certain amount also forms methane, probably by way of the free radical HC⋮ (Bone and Coward, *J.C.S.*, 1908, **93**, 1197).

The composition of gaseous hydrocarbons.—When a measured volume of a gaseous hydrocarbon is mixed with a measured excess of oxygen and the mixture exploded in a eudiometer by a spark, water and carbon dioxide are formed:

$$C_mH_n + (m + \tfrac{1}{4}n)O_2 = mCO_2 + \tfrac{1}{2}nH_2O.$$

The water condenses to liquid on cooling and the carbon dioxide may be absorbed by potash solution, and hence its volume m found. The residual gas is the excess of oxygen, and hence the volume of oxygen $(m + \frac{1}{4}n)$ used to burn the hydrocarbon is found. The volume of oxygen used in burning the

hydrogen is $\frac{1}{4}n$. The molecular formula of the hydrocarbon is confirmed by the density. (See Partington and Stratton, *Intermediate Chemical Calculations*, Chap. III.)

EXAMPLE.—3·0 c.c. of ethylene mixed with 9·5 c.c. of oxygen gave on explosion 6·5 c.c. of gas, of which 6·0 c.c. were absorbed by alkali, leaving 0·5 c.c. of oxygen. Oxygen used = 9·5 − 0·5 = 9·0 c.c.

$m = 6{\cdot}0/3{\cdot}0 = 2$; $(m + \frac{1}{4}n) = 9{\cdot}0/3{\cdot}0 = 3$; $\therefore\ n = 4$. Hence the formula of ethylene is C_2H_4.

From a mixture of hydrocarbons, acetylene is absorbed by ammoniacal cuprous chloride solution (which also absorbs CO), ethylene by fuming sulphuric acid or bromine water, and the composition of the remaining gas may be found by explosion with oxygen.

A mixture containing x vols. of hydrogen H_2, y vols. of methane CH_4 and z vols. of ethylene C_2H_4 is exploded with excess of oxygen ; if d is the contraction after explosion, m the vol. of CO_2 formed and a the vol. of oxygen consumed, then :

$$d = \tfrac{3}{2}x + 2y + 2z,$$
$$m = y + 2z,$$
$$a = \tfrac{1}{2}x + 2y + 3z,$$

from which x, y and z can be calculated.

Coal gas.—The distillation of coal with formation of gas was carried out by the Rev. John Clayton in 1688, the results being published in 1739. It was also described by Bishop Watson (*Essays*, Cambridge, 1781, **2**, 317), who found that a permanent gas, tar, and a watery liquid were formed. The use of coal gas as an illuminant was introduced by William Murdoch in 1792 and in 1798 he installed a gas plant for lighting the factory of Boulton and Watt at Soho near Birmingham. Gas lighting was introduced into factories in 1805, the first public gas-works being in Salford, near Manchester, and about the same time gas lighting was used on a very small scale in London, the streets of which were partly lighted by gas in 1808, Paris following in 1815. The use of gas in houses came much later.

In gas-works (Fig. 206) bituminous coal is " carbonised " by heating at 700°–1000° in a row of horizontal fireclay *retorts*, heated by producer gas made by passing air and steam through red-hot coke. The coal gas passes by way of vertical iron *ascension pipes* into one long horizontal iron *hydraulic main*, which serves as a water-seal, preventing gas passing back when a retort is opened for charging with coal and removal of coke. In the hydraulic main partial separation into crude gas, ammoniacal liquor and tar occurs. The gas leaving the hydraulic main at about 60° contains the following impurities (which should subsequently be removed) in p.c. by volume :

Hydrogen sulphide -	0·9–1·7	Hydrocyanic acid -	0·05–0·15
Ammonia - - -	0·7–1·4	Carbon disulphide -	0·02–0·04

More tar, and ammoniacal liquor, separate in the *condensers*, a series of air or water-cooled iron pipes, the two liquids passing into the *tar well*. After

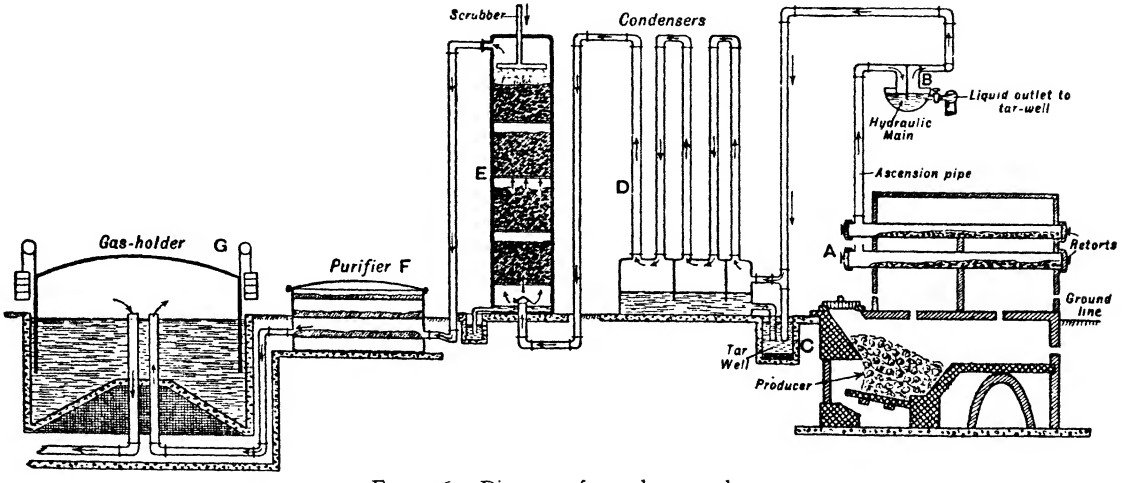


FIG. 206.—Diagram of a coal gas-works.

On the right two banks of horizontal fire-clay retorts *A* are shown in section. They are fitted with doors at each end to facilitate removal of the coke, and are heated to about 700° by gas made in the gas-producer shown below. The crude gas from the retorts passes to the hydraulic main, shown in cross-section at *B*, in which it is cooled to about 60°, and the liquid which separates passes to the tar-well *C*. The gas then passes through the air- or water-cooled pipes of the condensers *D*, in which it is cooled to atmospheric temperature and as a result more tar and ammoniacal liquor are separated and pass into the tar-well. After passing through exhausters and a tar-separator (not shown in the figure) the gas passes through washers or scrubbers *E*, the type shown being an iron tower containing coke packed in sections, over which a stream of water is passed downwards, the gas passing upwards. The washed gas then passes through the purifiers *F*, containing hydrated ferric oxide, in which the hydrogen sulphide is removed. The purified gas then passes into the gas-holder *G*, the one shown being of the wet type and drawn on a much smaller scale than the rest of the apparatus.

cooling, the gas passes to the *exhausters*, which maintain a slightly reduced pressure back to the retorts and force the gas forwards through the subsequent purifiers into the gas-holder. From the exhausters the gas passes to a *tar separator* in which tar fog is taken out, say by dividing the gas into fine streams which impinge on a solid surface to which the tar droplets adhere.

The gas then passes to a *washer*, which may be an iron tower packed with coke or boards set on edge, over which water runs in the opposite direction to the gas flow. Large rotary washers with revolving brushes dipping into water are also used.

The scrubbed gas still contains as impurities upwards of 400 grains of sulphur per 100 cu. ft. in the form of hydrogen sulphide and 40 grains as carbon disulphide. It passes to the *purifiers*, which are iron boxes containing hydrated ferric oxide (" bog iron ore ") spread on shelves. This decomposes the hydrogen sulphide with formation of ferric sulphide :

$$2Fe(OH)_3 + 3H_2S = Fe_2S_3 + 6H_2O.$$

The oxide is " revivified " by exposure to air, when sulphur is separated and hydrated ferric oxide regenerated :

$$2Fe_2S_3 + 6H_2O + 3O_2 = 4Fe(OH)_3 + 6S.$$

It is usual to admit a small quantity of ammonia to the purifiers. When the " spent oxide " contains over 50 p.c. of free sulphur it is burnt and the sulphur dioxide formed used to make sulphuric acid.

In small works the hydrogen sulphide is absorbed by slaked lime :

$$Ca(OH)_2 + 2H_2S = Ca(HS)_2 + 2H_2O.$$

In this case, carbon disulphide vapour is removed from the gas by passage over " foul lime " from the purifiers, when calcium thiocarbonate is formed, and the hydrogen sulphide also liberated is taken out in a second lime purifier :

$$Ca(HS)_2 + CS_2 = CaCS_3 + H_2S.$$

If hydrated iron oxide is used to remove hydrogen sulphide the carbon disulphide is usually left in the gas : it may be removed by a catalytic process in which the gas (containing free hydrogen) is passed over nickel at 430°, the hydrogen sulphide formed being removed as usual : $CS_2 + 2H_2 = C + 2H_2S$.

The purified gas passes to a *gas-holder*, which in the " wet-type " is a large counterpoised iron bell sealed below by water, and in the " dry-type " is an iron tower with a piston sealed by tar flowing round the edge. In many works the gas is dehydrated after purification by passing through concentrated calcium chloride solution and the water in a wet gas-holder is then covered with a layer of suitable oil to prevent re-wetting of the gas.

The purified gas must, according to law, contain less than 1 pt. of H_2S in 10 millions, *i.e.* it must not, when passed at 5 cu. ft. per hour, blacken lead acetate paper in 3 minutes. It is allowed, however, to contain carbon disulphide vapour which is just as objectionable, forming sulphur dioxide on combustion and thus causing corrosion of metal and vitiation of the atmosphere. The

presence of 0·05 pts. per million by vol. of nitric oxide in the gas causes gum formation with unsaturated hydrocarbons.

Carbonisation in large works is now generally carried out in large narrow vertical retorts of silica brick, more or less steam being introduced below to the retort; the coke cooled by the steam is extracted continuously from the bottom of the retort, the coal being fed continuously to the top. The coal gas mixes with water gas formed by the action of steam on the red-hot coke: $C + H_2O \rightleftharpoons CO + H_2$. Even with horizontal retorts the gas is frequently mixed with water gas made separately.

Liquid purification systems may be used. In one, hydrogen sulphide (with carbon dioxide and hydrocyanic acid) is absorbed in sodium carbonate solution, the hot solution being exposed to a current of air, which reverses the absorption reactions:

$$Na_2CO_3 + H_2S \rightleftharpoons NaHS + NaHCO_3,$$
$$Na_2CO_3 + CO_2 + H_2O \rightleftharpoons 2NaHCO_3,$$
$$Na_2CO_3 + HCN \rightleftharpoons NaCN + NaHCO_3.$$

In the *Thylox process* a solution of sodium or ammonium thioarsenate at 45° is used, the resulting solution being oxidised by a current of air:

$$(NH_4)_3AsO_2S_2 + H_2S = (NH_4)_3AsOS_3 + H_2O,$$
$$2(NH_4)_3AsOS_3 + O_2 = 2(NH_4)_3AsO_2S_2 + 2S.$$

Other processes involve the absorption of hydrogen sulphide in triethanolamine $N(C_2H_4OH)_3$ or in sodium phenoxide C_6H_5ONa solution; in both cases the hydrogen sulphide is driven out again by steam.

Hydrocyanic acid is recovered from the crude gas either as *ferrocyanide* by passing through a washer containing an alkali and an iron salt:

$$FeSO_4 + H_2S = FeS + H_2SO_4,$$
$$FeS + 6HCN + 2K_2CO_3 = K_4Fe(CN)_6 + H_2S + 2CO_2 + 2H_2O,$$

or as *ammonium thiocyanate* by passing through a washer containing ammoniacal liquor to which powdered sulphur is periodically added:

$$(NH_4)_2S_2 + HCN = NH_4CNS + NH_4HS,$$
$$NH_4HS + NH_3 + S = (NH_4)_2S_2.$$

Potassium ferrocyanide is made from spent oxide, containing Prussian blue, by heating with milk of lime, precipitating $CaK_2[Fe(CN)_6]$ from the solution of calcium ferrocyanide by adding potassium chloride, and decomposing with potassium carbonate: $CaK_2[Fe(CN)_6] + K_2CO_3 = CaCO_3 + K_4Fe(CN)_6$.

The average volume percentage composition of unmixed purified coal gas is:

Hydrogen	38 – 55	*Diluents*, non-illuminating but heat-producing.
Methane	22 – 25	
Carbon monoxide	4 – 15	
Ethylene, acetylene and benzene	2·5 – 5	*Illuminants*, unsaturated hydrocarbons.
Nitrogen (mostly from air leakage)	2 – 20	*Inerts.*
Carbon dioxide	0 – 3	
Oxygen	0 – 1·5	

The calorific value of coal gas is about 450 to 560 B.Th.U. per cu. ft. gross (to *liquid* water). The gas is sold on its heating value in *therms* (1 therm = 100,000 B.Th.U.).

The luminosity of coal gas flames is due to the 3 p.c. of ethylene and its homologues (*olefins*), the 0·06–0·07 p.c. of acetylene, and benzene vapour (this is now generally removed from the gas and recovered). Since gas is now burnt with mantles its illuminating power is of little importance.

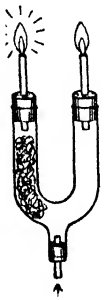


FIG. 207.—Luminosity imparted to hydrogen flame by toluene vapour.

EXPT. 6.—Fit a brass blowpipe jet to each arm of a Y-tube, in one arm of which is a piece of cotton-wool soaked in toluene (Fig. 207). Pass hydrogen through and kindle the two jets. The hydrogen saturated with toluene vapour burns with a luminous flame.

In America natural gas (CH_4), and liquefied and compressed propane and butane gases from petroleum, are largely used.

Coke.—The red-hot residue of gas coke in the retorts is raked out or pushed out by rams through doors opened at the front and back, and quenched with water. It contains all the ash of the coal, about half the sulphur, and small quantities of nitrogen, hydrogen and oxygen. The average percentage of carbon is 81.

The average yields from 1 ton of Newcastle coal in gas-making are: 12,500 cu. ft. of gas, 1 gallon of light oil scrubbed from the gas, 110 lb. of tar yielding 77 lb. of pitch, 7 lb. of ammonia, and 65–70 p.c. of the weight of the coal as coke.

A hard metallurgical coke (*e.g.* for blast furnaces) is prepared in **coke-ovens.** The old " beehive " oven was a mound of brickwork, in which the coal partly burnt in a limited supply of air as in charcoal burning. The high temperature carbonised the rest of the coal and all the volatile products were lost. In modern " recovery ovens," *e.g.* the Otto, Simon-Carvès or Koppers ovens, the coal is heated in closed fireclay or silica-brick retorts, 40 ft. long, 14–18 in. wide and 12 ft. 6 in. high (Fig. 208), by flues passing between them in which part of the gas evolved, mixed with air preheated in regenerators, burns. The oven gas is cooled to separate tar and scrubbed with creosote or other oil to recover benzene, and surplus gas is sold to gas companies. The coke is pushed out by rams and quenched with water.

" Low temperature carbonisation " aims at treating bituminous coal at a temperature of 425°–760° C. instead of 1000° as in ordinary gas works or coke ovens. A ton of coal then gives about 14 cwt. of smokeless free-burning fuel, together with 1½ gallons of crude light oil, 15–20 gallons of tar (which is different in composition from high temperature tar) and 3500–6000 cu. ft. of gas of calorific value 650–800 B.Th.U. per cu. ft.

Crude benzene (" benzol ") is extracted from coal gas or coke-oven gas by washing with a suitable oil, or by adsorption on charcoal. This reduces the

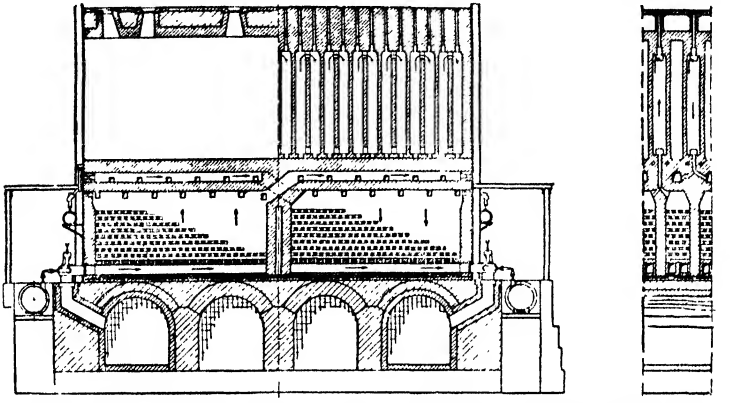


FIG. 208.—Koppers coke-oven with " hair-pin " circulation flues and cross-over regenerator.
Courtesy of Coke Oven Managers' Association and Dr. R. A. Mott.

carbon disulphide and sulphur compounds in the gas by half, and also takes out about 95 p.c. of the naphthalene. The naphthalene in gas tends to be deposited in pipes, causing stoppages.

FLAME AND COMBUSTION

A *flame* is a zone in which chemical reaction between gases is occurring, accompanied by the evolution of heat and light : briefly, it is glowing gas (Van Helmont, 1648 ; the definition goes back to Aristotle ; Partington, *Nature*, 1935, **135**, 916). Transparent gases such as nitrogen or oxygen do not glow when heated in tubes to a high temperature, nor do burning solids emit flame unless a gas or vapour is formed.

Flame is produced in chemical reactions liberating much energy, and the emission of light is due to chemical reactions. **Chemiluminescence** may be regarded as a cold flame. The glow of phosphorus is a familiar example and if ether is dropped on a hot iron plate a greenish phosphorescent flame is seen. Chemiluminescence is also shown in solution.

EXPT. 7.—Add 30 c.c. of 30 p.c. hydrogen peroxide in a dark room to a mixture of 10 c.c. of 10 p.c. pyrogallol solution, 20 c.c. of saturated potassium carbonate solution, and 10 c.c. of commercial formaldehyde. An orange-red glow accompanied by a vigorous reaction is seen. Light of the wave-length emitted is found to accelerate the reaction, which involves the oxidation of pyrogallol (Trautz, *Z. Elektrochem.*, 1905, **53**, 1).

Unless the combustible gas and supporter of combustion are mixed before kindling, the *flame is hollow* and fills only the surface of contact of the two gases.

Francis Bacon (*Sylva Sylvarum*, 1615) held an arrow for a short time across a candle-flame and found that the wood inside the flame was " as if the fire had scarce touched it." Hooke (*Micrographia*, 1665; *Lampas*, 1677) held a thin sheet of glass [mica is better] across a candle-flame and noticed the dark central spot due to unburnt gas: " all the middle of the cone of flame neither shines nor burns, but only the outer superficies thereof that is contiguous to the free and unsatiated air," which " preyeth upon those parts of it that are outwards." He thus recognised the part played by the air.

EXPT. 8.—Depress a piece of new asbestos paper on a Bunsen flame: a hollow dark ring is formed by the section of the flame.

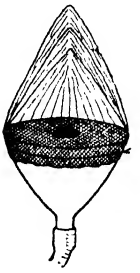


FIG. 209.—Experiment to demonstrate that a flame is hollow.

EXPT. 9.—Support a match head upwards in the tube of a Bunsen burner by a pin stuck through it, and kindle the flame. The match-head does not ignite for a considerable time.

EXPT. 10.—Stretch a piece of fine wire gauze over a funnel and place a *small* heap of gunpowder in the centre (Fig. 209). Pass a rapid stream of coal gas through the funnel, and kindle the gas from above. The powder remains in the centre of the flame, but it ignites if the flame is slowly turned down.

EXPT. 11.—Insert one end of a glass tube into the middle portion of a Bunsen flame. Unburnt gas may be kindled at the upper end of the tube.

The functions of the **combustible** and **supporter of combustion** are interchangeable, and depend on which gas is inside and which outside the flame. In ordinary flame combustion processes, which occur in the atmosphere, a gas such as hydrogen or coal gas burns in air, the oxygen of which reacts with the combustible gas. Oxygen gas, however, will burn with a flame equally well in an atmosphere of hydrogen (p. 655) or coal gas, and the combustion of hydrogen and chlorine is interchangeable with a combustion of chlorine in hydrogen (p. 755). When air burns in an atmosphere of hydrogen or coal gas, only the oxygen reacts, not the nitrogen, but the air-flame is just as correctly described as " air burning in coal gas " as the ordinary flame is spoken of as " coal gas burning in air."

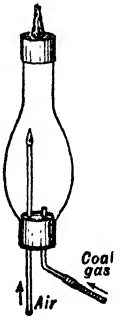


FIG. 210.—Air burning in coal gas.

EXPT. 12.—A lamp chimney with a brass or tin-plate top (Fig. 210) is fitted with tubes as shown. Coal gas is passed in and kindled at the top. At the same time air is drawn in through the second tube, and if a lighted taper is passed through this tube into the chimney the oxygen of the air burns in the coal gas with a blue non-luminous flame. A taper passed down from above to the air-flame cannot be kindled, since it is surrounded by an atmosphere of coal gas, but a jet of air ignites.

If the supply of gas is reduced the upper flame shrinks and becomes less luminous, whilst the lower flame increases in size, since the oxygen has now less coal gas available, and the combustion extends over a larger space.

EXPT. 13.—Arrange a glass cylinder with two tubes as shown in Fig. 211. Pass coal gas through *A* and kindle a large flame at the top. Push *B* into this flame and pass in a slow stream of oxygen. A flame of oxygen is seen burning inside the first flame, the oxygen reacting with the unburnt gas in the centre of the hollow flame. If *B* is lowered, the oxygen flame continues to burn in the atmosphere of coal gas.

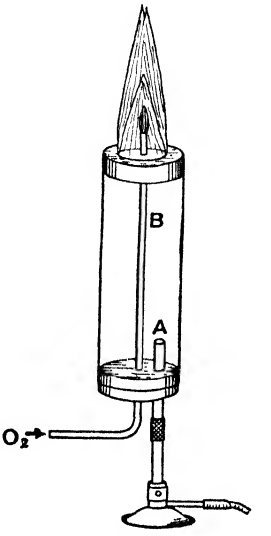


FIG. 211.—Oxygen burning inside a coal gas flame.

A candle or oil-lamp has a cotton wick surrounded by melted wax or liquid oil, which rises in the wick by capillary attraction. The top of the wick becomes incandescent and the fuel decomposes, the combustible gas burning with a flame.

EXPT. 14.—Attempt to kindle a piece of lump-sugar by a taper: the sugar melts but will not take fire. Now rub a corner of the sugar with a small quantity of tobacco ash: the sugar can readily be lighted at that point and burns with a flame.

The wick of a modern candle is plaited so that it bends over and is continuously consumed in the outer part of the flame. The wick presents the combustible material to the heated zone owing to its capillary structure, and it prevents too rapid conduction of heat from the heated point.

The structure of flame.—A *hydrogen* or *carbon monoxide flame* burning in air or oxygen (Fig. 212) has *two* cones, an inner *A* of unburnt gas and an outer

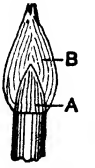


FIG. 212.—Structure of hydrogen or carbon monoxide flame (two cones).

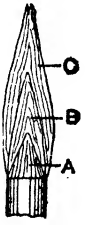


FIG. 213.—Structure of ammonia flame (three cones).

B, in which the single overall reaction: $2H_2 + O_2 = 2H_2O$ or $2CO + O_2 = 2CO_2$ occurs. A flame of pure hydrogen burning from a metal jet in dust-free air does not emit a visible light. The *ammonia flame* in oxygen (Fig. 213) has *three* cones, an inner *A* of unburnt gas, a yellow cone *B* in which decomposition of ammonia is taking place: $2NH_3 = N_2 + 3H_2$, and an outer pale greenish-

yellow cone *C* in which the hydrogen burns. A flame of *hydrogen sulphide*, *carbon disulphide* vapour, or *cyanogen* in oxygen or air is similar:

$$2H_2S + O_2 = 2H_2O + 2S \text{ in } B; \qquad 2CS_2 + O_2 = 2CO + 4S \text{ in } B;$$
$$S + O_2 = SO_2 \text{ in } C; \qquad 2CO + 4S + 5O_2 = 4SO_2 + 2CO_2 \text{ in } C.$$

In the cyanogen flame the cone *B* is pink and corresponds with the reaction: $C_2N_2 + O_2 = 2CO + N_2$, whilst the cone *C* is greenish and represents the combustion of the carbon monoxide: $2CO + O_2 = 2CO_2$.

Hydrocarbon flames contain *four* regions first clearly defined by Berzelius (*The Use of the Blowpipe*, 1822; Smithells, *J.C.S.*, 1892, **61**, 217) (Fig. 214):

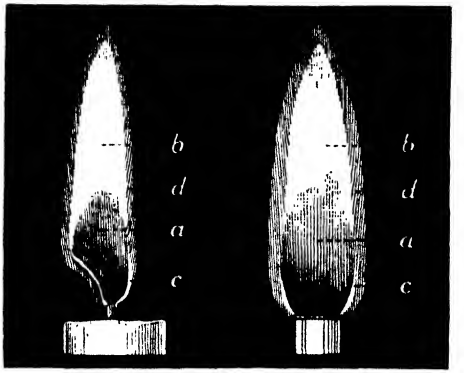


FIG. 214.—Structure of hydrocarbon flames.

(*a*) the dark inner cone of unburnt gas or wax vapour, (*b*) a yellowish-white brightly luminous region, occupying most of the flame, (*c*) a small bright blue cup-shaped region at the base, (*d*) a faintly-visible outer mantle, completely surrounding the flame. The reactions in the parts of hydrocarbon flames are discussed on p. 468.

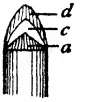


FIG. 215.—Small hydrocarbon flame with continuous blue region *c*.

If the supply of gas is reduced the flame shrinks, the luminous area *b* gradually disappearing whilst the region *c* becomes continuous and forms an inner cone (Fig. 215).

Davy's researches on flame.—Sir Humphry Davy in 1815 (*Works*, 1840, vol. 6) was led to study flame in an investigation of the causes and prevention of fire-damp explosions in coal mines, which are caused by the kindling of mixtures of methane (*fire-damp*) and air, or (as we now know) sometimes of mixtures of very fine coal-dust with air. Davy in a series of masterly experiments found that if a flame is cooled it is extinguished, and he recognised that combustible gases have different **ignition points**, that of methane being high (700°) so that it is not kindled by red-hot metal.

EXPT. 15.—Lower a close spiral of thick copper wire over a *small* night-light flame: this is extinguished.

EXPT. 16.—(i) Depress fine wire gauze over a Bunsen flame. The flame does not pass owing to the cooling by conduction through the metal, and a red-hot ring is seen with a dark centre where unburnt gas is passing through the gauze. This may be kindled by a lighted taper above. If the gauze remains on the flame too long, the temperature of the metal rises to the ignition point of the gas.

(ii) A piece of gauze turned up at the edges is held over an unlighted burner; the gas passing through may be kindled above but the non-luminous flame does not pass through. On raising the gauze, the flame finally goes out (Fig. 216).

FIG. 216.—Principle of safety lamp.

As a result of his experiments Davy invented the **safety lamp**, which (Fig. 217A) is a small oil lamp with the flame enclosed in a cylinder of wire gauze. In the modern form (Fig. 217B) the lower part is a strong glass cylinder, the gauze above this being shielded by an aluminium "bonnet." The lamp wick is adjusted by a wire passing down through the brass lamp, which is firmly screwed to a brass collar supporting the glass chimney and upper part of the lamp. Fire-damp can penetrate and burn inside the gauze, but the flame is not propagated because the heat is conducted away by the gauze, which may even become red-hot. A draught of air on the lamp may cause the gauze to become so hot as to kindle the fire-damp, and the flame may also be blown mechanically through the gauze by a blast of air moving faster than 8 ft. per sec., such as is formed on firing a shot. With these exceptions the lamp is perfectly safe. If only a small amount of fire-damp is present, a *flame-cap* appears over the flame of the lamp, and from the size of this the amount of combustible gas may be estimated.

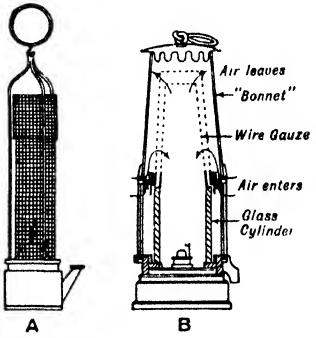


FIG. 217.—Safety lamp.
Reproduced from Mellor's Modern Inorganic Chemistry (Longmans).

EXPT. 17.—Lower a lighted Davy lamp into a large beaker into which some ether has been poured. The ether vapour-air mixture extinguishes the flame, but burns outside the lamp when kindled by a taper. The lamp may also be hung inside a large bell jar into which coal gas is passed.

Ignition points.—Different combustible gases have different temperatures of ignition (*ignition points*) in air or oxygen, as is seen from the table below. The limits found by different methods are sometimes rather wide. In some cases the ignition points in air and oxygen are nearly the same, in others that in air is higher than that in oxygen.

The *flash point* of a liquid fuel is the temperature at which it emits a vapour which is kindled by a flame.

Ignition temperatures				
Gas	In oxygen	Mean	In air	Mean
H_2 - -	580°–590°	585°	580°–590°	585°
CO (moist) -	637°–658°	650°	644°–658°	651°
C_2H_4 - -	500°–519°	510°	542°–547°	543°
C_2H_2 - -	416°–440°	428°	406°–440°	429°
CH_4 - -	556°–700°	626°	650°–750°	700°
C_2N_2 - -	803°–818°	811°	850°–862°	856°

Mixtures of air and inflammable gas will propagate flame only when their compositions are between certain *limit mixtures*, containing the minimum and maximum volume percentages of combustible gas. These vary somewhat with the conditions of combustion ; the figures in the table below are for mixtures burning upwards in a 7·5 cm. diameter glass tube. The wide limits for acetylene have already been mentioned (p. 455).

	Lower limit vol. p.c.	Upper limit vol. p.c.
H_2 - - - - -	4·1	75
CO - - - - -	12·8	72
CH_4 - - - - -	5·35	14·85
C_2H_4 - - - - -	3·02	3·40
C_2H_2 - - - - -	2·60	80·5
CS_2 - - - - -	1·06	50·0

Le Chatelier found that when two limit mixtures of different gases (both upper or both lower) are mixed, the resulting mixture is also a limit mixture.

Luminosity of Flame

Davy's theory.—Davy in 1816 explained the luminosity of a hydrocarbon flame as due to the incandescence of solid particles of carbon produced in the flame by thermal decomposition of the combustible gas :

" . . . the decomposition of a part of the gas towards the interior of the flame, where the air was in smallest quantity, and the deposition of solid charcoal, which first by its ignition and afterwards by its combustion, increases to a high degree the intensity of the light."

Flames containing solid particles, such as flames of zinc, magnesium and potassium in oxygen, are luminous. The presence of solid carbon particles in luminous hydrocarbon flames was proved by Soret (*Compt. rend.*, 1874, **78**, 1299), who showed that a powerful beam of sunlight reflected from a candle flame is polarised, and this was confirmed by Burch (1885) and Stokes (1891) ; arc light has also been used. Polarisation is characteristic of light scattered by turbid media (p. 84).

Expt. 18.—Clouds of soot from burning camphor admitted through one air-hole of a Bunsen burner by a funnel tube make the flame luminous (Fig. 218).

EXPT. 19.—In Faraday's experiment (*The Chemical History of a Candle*, 1886, p. 44) a rather wide glass siphon is lowered into a candle flame just above the wick. Dense white vapours of volatilised wax pass over into a small flask (Fig. 219). On raising the tube into the bright part of the flame, dense black vapours pass over, which deposit particles of carbon in the flask. On raising the tube still further, the black smoke disappears, steam and carbon dioxide pass along the siphon, and the gas turns lime water in a flask milky.

Frankland's theory.—Sir Edward Frankland in 1861 (*Phil. Trans.*, 1861, **151**, 629; *Proc. Roy. Soc.*, 1868, **16**, 419; *Experimental Researches*, 1877, 863, 905) noticed that the luminosity of a candle flame on the summit of Mont Blanc is much feebler than in the valley at Chamonix, although the rate of combustion is unchanged. In further experiments he showed that a candle or coal-gas flame burning in a partly exhausted receiver is much less luminous than in free air (this had been noticed by Boyle), and that an alcohol flame burning in air at 4 atm. pressure is luminous (this had been stated by Davy in 1817).

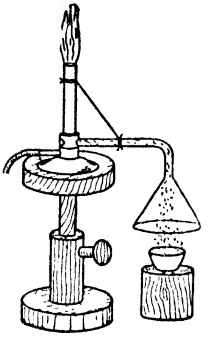


FIG. 218.—Bunsen flame rendered luminous by smoke from burning camphor.

A mixture of hydrogen and oxygen kindled in a eudiometer burns with a bright flash, and hydrogen burning in oxygen under 20 atm. pressure gives a luminous flame. The luminosity of the electric spark in gases increases with the density of the gas. Luminous flames are known in which solid particles cannot be present, *e.g.* flames of phosphorus and arsenic in oxygen, carbon disulphide in oxygen (or a mixture of carbon disulphide vapour and nitric oxide), and sodium in chlorine. Frankland suggested that the luminosity of hydrocarbon flames is due to incandescent *dense* but transparent *hydrocarbon vapours*. The presence of solid carbon particles in luminous hydrocarbon flames has, however, been proved, although Frankland's theory may apply to flames in which solid particles cannot be present.

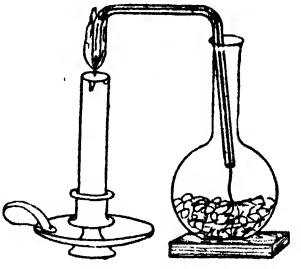


FIG. 219.—Faraday's experiment.

Lewes' theory.—By aspirating and analysing the gas from different parts of a hydrocarbon flame, V. B. Lewes (*J.C.S.*, 1892, **61**, 322; cf. Smithells, *ibid.*, 1895, **67**, 1049) found that the unsaturated hydrocarbons (ethylene and acetylene) disappear only slowly in the dark portion, but rapidly in the luminous zone. The proportion of acetylene increases rapidly as the gas passes up the dark zone, attaining 70 p.c. of the unsaturated hydrocarbons at the apex of the dark cone,

although only 1·41 p.c. of these hydrocarbons are present. Lewes assumed that hydrocarbons are decomposed by heat with the intermediate formation of acetylene : $2CH_4 = C_2H_2 + 3H_2 = 2C + 4H_2$. Free hydrogen has been detected in the luminous zone. The carbon separates as a fine powder and the heat of decomposition of the endothermic acetylene assists in raising the temperature.

Reactions in Hydrocarbon Flames

If the luminosity of hydrocarbon flames is due to incandescent solid particles of carbon, as seems definitely proved, it has still to be explained how these are formed.

Davy believed (p. 466) that the carbon is formed by the *thermal decomposition* of hydrocarbons by the heat of the flame. Early in the nineteenth century an alternative theory was proposed, which for long afterwards was taught as the most probable one. This is the theory of the *preferential combustion of hydrogen* ; it states that oxygen has a greater affinity for hydrogen than for carbon, so that when a hydrocarbon at a high temperature is attacked by insufficient oxygen to burn it completely, the hydrogen burns to steam and the carbon separates in the free state.

Although this theory was given before by Liebig (*Annalen*, 1839, **30**, 250), Graham (*Elements of Chemistry*, 1842, 420 ; 2nd edit., 1850, **1**, 382), and Fownes (*Manual of Chemistry*, 1844, 157), it is generally attributed to Faraday, who (*Lectures on the Non-Metallic Elements*, 1853, 280) says of a candle flame :

" The volatile matter is a vapour composed of carbon and hydrogen ; and the forces which hold these elements together are so nicely balanced that the hydrogen is made to combine first, the carbon afterwards."

Dalton in 1805 (*New System of Chemical Philosophy*, 1810, **1**, ii, 442, 448), however, had found that :

when methane is mixed with its own volume of oxygen, " the least that can be used with effect," and fired by an electric spark, the mixture explodes without appreciable change in volume with formation of carbon monoxide and hydrogen : $CH_4 + O_2 = CO + H_2 + H_2O$. " Each atom of gas requires only 2 atoms of oxygen ; the one joins to one of hydrogen and forms water [HO according to Dalton] ; the other joins to the carbone to form carbonic oxide, and at the same moment the remaining atom of hydrogen springs off." On adding a further volume of oxygen, the gas may again be fired by a spark : $CO + H_2 + O_2 = CO_2 + H_2O$.

When ethylene is exploded with its own volume of oxygen all the carbon burns to carbon monoxide and all the hydrogen is set free : $C_2H_4 + O_2 = 2CO + 2H_2$.

Dalton's experiments point to a preferential combustion of carbon rather than hydrogen, but were overlooked until Kersten in 1861, from similar experiments, concluded that :

" Before any portion of the hydrogen is burnt all the carbon is burnt to carbon monoxide, and the excess of oxygen divides itself between the carbon monoxide and the hydrogen."

The oxidation reaction in a hydrocarbon flame was thus interpreted as a *preferential combustion of carbon*, and Davy's theory of thermal decomposition was held to explain the deposition of carbon.

A *hydroxylation theory* of hydrocarbon combustion (van't Hoff, *Ansichten über die organische Chemie*, 1879, **1**, 168; H. E. Armstrong, *J.C.S.*, 1903, **83**, 1088) assumes that the oxidation of a hydrocarbon occurs by the entrance of oxygen into the molecule, where it is distributed between the carbon and hydrogen, giving unstable hydroxylated molecules which, in turn, undergo oxidation or thermal decomposition:

$$\underset{\text{methane}}{CH_4} \rightarrow \underset{\text{methyl alcohol}}{CH_3OH} \rightarrow \underset{\text{unknown in free state}}{CH_2(OH)_2} \rightarrow \underset{\text{formaldehyde}}{H\cdot CHO} \rightarrow \underbrace{H\cdot COOH}_{\text{formic acid}} \rightarrow \underbrace{HO\cdot CO\cdot OH}_{\text{carbonic acid}}$$

$$\underbrace{\qquad\qquad}_{CO + H_2O} \qquad \underbrace{\qquad\qquad}_{CO_2 + H_2O}$$

The theory is supported by experiments on the *slow oxidation* of hydrocarbons (Bone, etc., *J.C.S.*, 1902–6; 1933, 1599; *Phil. Trans.*, 1915, **215**, 275). At 360° and 100 atm. pressure up to 17 p.c. of methane may be oxidised rapidly to methyl alcohol, with only 0·6 p.c. to formaldehyde and no trace of hydrogen peroxide. Under ordinary conditions formaldehyde is the first product detected.

The combustion of ethylene is represented as follows:

$$\underset{\text{ethylene}}{H_2C:CH_2} \rightarrow \underbrace{CH_2:CH(OH)}_{\text{vinyl alcohol}} \rightarrow \underbrace{(HO)\cdot CH:CH(OH)}_{\text{hypothetical}}$$

$$\underbrace{CH_3\cdot CHO}_{\text{acetaldehyde}} \qquad \underbrace{2H\cdot COH}_{\text{formaldehyde}} \rightarrow \underbrace{H\cdot COOH}_{\text{formic acid}} \rightarrow \underbrace{HO\cdot CO\cdot OH}_{\text{carbonic acid}}$$

$$\underbrace{\qquad\qquad}_{H_2O + CO} \qquad \underbrace{\qquad\qquad}_{H_2O + CO_2}$$

and the combustion of acetylene (Bone and Andrew, *J.C.S.*, 1905, **87**, 1232; Lenher, *J.A.C.S.*, 1931, **53**, 3737):

$$\underset{\text{acetylene}}{HC:CH} \rightarrow \underbrace{(HC:O)_2}_{\text{glyoxal}}$$

$$\underbrace{CO + H\cdot COH}_{\text{formaldehyde}} \rightarrow \underbrace{H\cdot COOH}_{\text{formic acid}} \rightarrow \underbrace{HO\cdot CO\cdot OH}_{\text{carbonic acid}}$$

$$\underbrace{\qquad\qquad}_{H_2O + CO} \qquad \underbrace{\qquad\qquad}_{H_2O + CO_2}$$

Bone postulated similar reactions in flames. The production of hydrogen in incomplete explosive combustion is considered to be due to secondary thermal decomposition of formaldehyde: $HCOH = H_2 + CO$, and the solid carbon from an alternative decomposition of acetaldehyde: $CH_3\cdot CHO = C + 2H_2 + CO$.

The spectrum of the inner cone of the Bunsen flame shows the presence of the radicals C_2 (giving the green "Swan bands"), OH ("steam bands") and CH (violet-blue bands), and those of hydrocarbon flames C_2 and CH radicals, and these are probably formed by *chain reactions*.

Callendar (1927) supposed that *unstable peroxides* are first formed from hydrocarbons and oxygen and then decompose, the products being further oxidised by excess of oxygen to oxides of carbon and steam (Ellis and Kirkby, *Flame*, 1936; Lewis and von Elbe, *Combustion, Flame and Explosion in Gases*, Cambridge, 1938; Jost, *Explosions- und Verbrennungsvorgänge in Gasen*, Berlin, 1939; Norrish, *Proc. Roy. Soc.*, 1935, **150**, 36; 1936, **157**, 503).

The Bunsen Flame

Coal gas mixed with sufficient air *before* combustion, as in the familiar Bunsen burner (1853), burns with a non-luminous flame with *two cones*: (1) a pale blue inner cone, which becomes green and shrinks when a large supply of air is admitted (as in Teclu and Meker burners), (2) a paler blue outer cone, which remains constant in size. The reactions in the inner cone differ from those in a luminous flame, since oxidation occurs with formation of carbon monoxide and hydrogen, which burn in the outer cone.

The effect of admixture of air on the flame may be studied with the apparatus shown in Fig. 220. Undiluted carbon monoxide burns with a hollow cone of

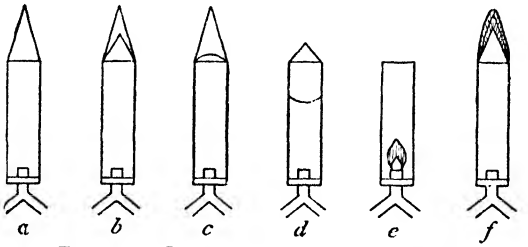


Fig. 220.—Smithells' experiment on flames.

blue flame (*a*), typical of a *volume flame*. If a little air is admitted the cone becomes shorter and its inner lining bright blue (*b*). With more air a mixture is produced through which a flame would propagate without external air, but the flame is kept on the top of the tube by the speed of the gas current (*c*). More air gives a speed of propagation of flame greater than the speed of the gas current, and the inner cone separates and passes down the tube (*d*). With more air the outer cone vanishes, and all the gas burns in the inner cone (*e*). The rate of propagation of flame has now been diminished by the excess of air, and the lower flame is a double cone as in the first case. When the rate of inflammation is reduced below the rate of flow of gas, the flame again rises to the top of the tube (*f*) and burns as a single cone with a considerable unburnt inner space, typical of a *surface flame*.

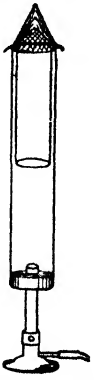


Fig. 221.—Separation of cones of Bunsen flame.

Expt. 20.—The two cones of a Bunsen flame may be separated (Dixon, 1887, *q.* by Smithells, *Nature*, 1893, **49**, 86; Teclu, *J.C.S.*, 1891, **60**, 1309) by fixing a wide glass tube over a large Bunsen burner, lighting the flame at the top, and slowly increasing the air supply (Fig. 221). The inner cone passes separately down the tube and may be stopped (owing to cooling by conduction) by a ring of copper wire in the wide tube. By an exact adjustment of air, the inner cone alternately sinks and rises in the tube.

Expt. 21.—The separation of the flame cones is also effected by **Smithells' flame-cone separator** (*J.C.S.*,

1892, **61**, 204; 1894, **65**, 603). This consists (Fig. 222) of a glass tube sliding inside a wider tube, both having metal rims. A mixture of air and coal gas passes into the central tube. If the air supply is increased, the Bunsen flame at the top separates into two cones, one of which remains on the outer tube and the other, which is the inner cone of the complete flame, passes down and burns on the top of the narrower tube. By starting with the inner tube at the top and drawing it down, the complete flame is separated, and is formed again by raising the inner tube.

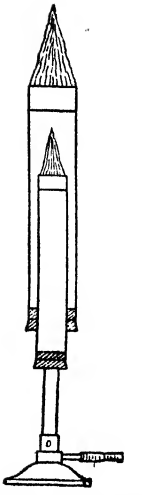


FIG. 222.—Smithells' flame-cone separator.

The gas between the separated cones in Smithells' apparatus consists of nitrogen (from air), carbon monoxide, carbon dioxide, steam and hydrogen. The composition is qualitatively the same if pure methane, ethylene, or benzene vapour is used instead of coal gas. A *water-gas equilibrium* : $CO + H_2O \rightleftharpoons CO_2 + H_2$ is set up, and the law of mass action : $[CO][H_2O]/[CO_2][H_2] - K$ applies to this (Horstmann, 1877–79; Dixon, *Phil. Trans.*, 1884, **175**, 617; 1893, **184**, 97; 1903, **200**, 315). Haber and Richardt (1904) showed that it holds for the inter-conal flame gas, with a value of the equilibrium constant ($K = 3{\cdot}7$) corresponding with a temperature of 1500°.

The reaction in the bright blue part of a luminous flame (p. 464), where the combustible gas is in presence of free air, is the same as that in the inner cone of a Bunsen flame and the spectrum shows that C_2 radicals are present. In the outer, faintly visible, cone, complete combustion occurs, as in the outer cone of the Bunsen flame.

The **temperatures of flames** have been determined in various ways (*e.g.* by platinum and platinum-rhodium thermocouples) and the following values found (Féry, 1903, etc.) :

Bunsen, fully aerated	1871°	Oxy-coal gas blowpipe	2200°
,, insufficient air	1812°	Oxy-hydrogen ,,	2420°
,, alcohol	1862°	Oxy-acetylene explosion	3000°–4000°
Hydrogen in air	1900°	[Electric arc	3760°]
Alcohol flame	1705°	[Sun	7800°]
Acetylene flame	2548°		

Three explanations have been given for the **non-luminosity of the Bunsen flame** :

(1) **Oxidation** : Davy : all the carbon " is burnt in its gaseous combinations without previous deposition."

(2) **Dilution** : Knapp (1870) and Blochmann (1873–4) found that inert gases such as nitrogen, carbon dioxide and steam as well as air will render the flame non-luminous when mixed with the coal gas before combustion.

EXPT. 22.—Stop one air-hole at the base of a Bunsen burner and connect the other with a carbon dioxide apparatus. Light the coal gas and gradually admit

carbon dioxide : the flame becomes blue and non-luminous, but consists of only *one* cone.

Lewes (*J.C.S.*, 1892, **61**, 322) states that 1 volume of ordinary coal gas requires the following volumes of gases to make its flame non-luminous : CO_2 1·26, N_2 2·30, CO 5·11, H_2 12·4, air 2·27, O_2 0·5. The effect cannot be due entirely to cooling, as carbon monoxide gives a hotter flame than coal gas.

(3) **Cooling** : Wibel (1875) showed that a hydrocarbon flame becomes non-luminous when cooled, although solid carbon is not necessarily deposited.

EXPT. 23.—Bring a cold bright sand-bath in contact with the flame of coal gas burning at a fish-tail burner. The flame becomes non-luminous, but no soot is deposited.

Conversely, if the gas burning with a non-luminous flame at the top of a platinum or silica tube extension of a Bunsen burner is strongly heated by heating the tube to redness, the flame becomes somewhat luminous, although the composition of the gas mixture is not appreciably changed (Heumann, *Annalen*, 1876, **181**, 129 ; Thorpe, *J.C.S.*, 1877, **31**, 627).

EXPT. 24.—Two Bunsen burners with silica tube extensions are burnt side by side with flames made *just* non-luminous by sufficient air. One tube is heated by a blowpipe, when the flame is seen by comparison with that on the unheated tube to be slightly luminous.

In all probability oxidation, dilution and cooling all play a part in making the Bunsen flame non-luminous.

EXPLOSION AND DETONATION

The mixture of air and gas supplied to a Bunsen burner is explosive and the flame is prevented from striking down the tube only by keeping the upward speed of the gas current equal to the speed with which the flame would run down through the gas. By measuring the speed of the gas mixture Bunsen (1867) found that the speed of flame in a mixture of hydrogen and oxygen was 34 m. per sec. ; most other gases burn at the rate of about 1 m. per sec.

Experiments by Berthelot and Vieille (1881), Mallard and Le Chatelier (1881–83) and Dixon (1880–81 ; Bone and Townend, *Flame and Combustion in Gases*, 1927) showed, however, that if the explosive mixture is kindled (*e.g.* by an electric spark) at one end of a long tube, the flame first traverses a short length of the tube with a velocity comparable with Bunsen's figure, rapidly increases in speed to a maximum, and then flashes through the gas with a constant velocity very much higher than the initial velocity of the flame. This flame travelling with a high constant speed is called a **detonation wave.** The velocities of the detonation wave in various mixtures, determined by Dixon, are in m. per sec. :

$8H_2+O_2$	3535	$C_2N_2+O_2$	2728
$2H_2+O_2$	2821	$C_2N_2+2O_2$	2321
H_2+3O_2	1712	H_2+Cl_2	1729

The increased violence of combustion and the great speed of propagation of flame in the detonation wave may be shown by the following experiments ·

EXPT. 25.—(Le Chatelier): Fill a strong tube 2 in. wide and 5 ft. long, closed at one end with a rubber bung, with nitric oxide over water. Drain any water from the tube, insert another rubber bung, pour in a few c.c. of carbon disulphide, and shake. Support the tube vertically, take out the upper bung, and kindle the gas with a taper. The mixture burns noiselessly until the flame approaches the middle of the tube, and then flashes down quickly, with a peculiar howling noise as the detonation wave just begins. A glass screen should be placed before the lower part of the tube.

EXPT. 26.—(Dixon): A coil of lead pipe 30 ft. long and ¼ in. diameter is fitted at each end with brass coupling sockets as used for gas connections. To one of these a thin glass test-tube is attached by a rubber washer, and to the other by Faraday's cement a strong glass tube with firing-wires sealed through the glass and a stopcock above (Fig. 223). The coil is filled from a gas holder with a mixture $2CO + O_2$ containing a little hydrogen, the test-tube fixed in place and covered with a wire gauze cylinder. The tap is closed, and on passing a spark the test-tube is shattered by a loud explosion at the same instant as the flash is seen in the firing tube.

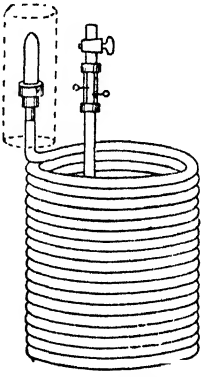


FIG. 223.—Velocity of detonation wave.

The nature of the detonation wave has been explained as follows (Jouguet, 1906; Dixon, *J.C.S.*, 1910, **97**, 661).

When burning is started, say by a spark, a compression wave spreads through the gas. In front of this wave the gas is at rest: at its crest it is completely burnt. Roughly speaking, the burning gas is driven forward bodily with the velocity with which sound travels in it, and the wave front runs through this moving gas with a velocity relative to the unburnt gas in front which is twice the velocity of sound in the burning gas. A detonation wave was "synthesised" by Bone and Fraser (1929) by following up a slow flame in a moist $2CO + O_2$ mixture by a shock wave transmitted through nitrogen to the mixture.

OXYGEN COMPOUNDS OF CARBON

Carbon dioxide CO_2, colourless gas, b.p. $-56°$ at 5·3 atm. pressure, sublimation temperature $-78·52°$, critical temperature 31·1°, critical pressure 72·85 atm.; the anhydride of **carbonic acid** HO·CO·OH.

Carbon monoxide CO, colourless gas, b.p. $-191\ 5°$, m.p. $-200°$, critical temperature $-138·7°$, critical pressure 34·6 atm.; the anhydride of **formic acid** H·CO·OH.

Carbon suboxide C_3O_2, colourless gas, b.p. $+6°$, m.p. $-111·3°$, the (double) anhydride of **malonic acid** $CH_2(COOH)_2$.

The solid oxides C_4O_3, C_8O_3 and $C_{12}O_9$ have also been described, and salts of the **percarbonic acids** H_2CO_4 and $H_2C_2O_6$ are known.

Carbon Dioxide

Carbon dioxide was first prepared by van Helmont about 1630, who called it *gas sylvestre*; it was examined by Joseph Black in 1755, who called it *fixed air*, and by Bergman in 1774. Lavoisier in 1783 showed that it is an oxide of carbon, determined its composition by burning charcoal and diamond in oxygen, showed (as had been discovered by Black) that it combines with bases, and called it *carbonic acid gas.*

Carbon dioxide issues in abundance from the earth in the Grotto del Cane (Naples), the Poison Valley (Java), and other places, and also mixed with nitrogen as *black damp* (or *chokc damp*) in mines. Asphyxiating gases from such sources, as well as that collecting in cellars, which extinguishes a candle, are mentioned by Pliny. Carbon dioxide is dissolved in many mineral waters (Moureu, *J.C.S.*, 1923, **123**, 1905), *e.g.* of Selters, Vichy, and the Geyser Spring of Saratoga. It is formed in respiration (as may be shown by blowing air from the lungs, containing about 4 p.c. by vol. of CO_2, through lime water, or baryta water, which becomes milky), in alcoholic fermentation: $C_6H_{12}O_6 = 2C_2H_5OH + 2CO_2$, and in other kinds of fermentation and the decay of organic matter.

Normal outdoor air contains about 3 volumes of carbon dioxide in 10,000. The average figures at Kew are 2·43 (min.) –3·60 (max.). On Mont Blanc the figures are 2·62 at an altitude of 1080 m. and 2·69 at an altitude of 3050 m. In crowded towns and especially in rooms not sufficiently ventilated the carbon dioxide may rise to 0·04–0·3 p.c. by vol.

The total amount of carbon dioxide in the atmosphere corresponds with about 600,000 million tons of carbon. Its sources are respiration of animals and plants, combustion, fermentation, putrefaction, the soil (worms, decay, and gas of volcanic origin), mineral springs, volcanic activity, and lime-burning. It is diminished by absorption by the sea (45 mg. CO_2 per litre), photosynthesis by green plants, and the weathering of rocks ($1{\cdot}62 \times 10^9$ tons of CO_2 per annum). On the whole, the carbon dioxide in the atmosphere appears to be slowly increasing.

In the estimation of atmospheric carbon dioxide by **Pettenkofer's method** a measured volume of standard baryta water is shaken with a known volume of air in a large (8–10 lit.) bottle, and the excess of baryta titrated with standard acid and phenolphthalein: $Ba(OH)_2 + CO_2 = BaCO_3 + H_2O$.

Carbon dioxide is prepared by the action of acids on carbonates:

$$2H^{\cdot} + CO_3'' \rightleftharpoons H_2CO_3 \rightleftharpoons CO_2 + H_2O.$$

Expt. 27.—Pieces of marble and dilute hydrochloric acid in a Woulfe's bottle or Kipp's apparatus are generally used: $CaCO_3 + 2HCl = CaCl_2 + CO_2 + H_2O$. The gas is washed with water or sodium bicarbonate solution to eliminate acid spray, and is collected by downward displacement, since it is 1·53 times as heavy as air. It may be dried by calcium chloride, sulphuric acid or phosphorus pentoxide.

Pure carbon dioxide is obtained by heating pure sodium bicarbonate: $2NaHCO_3 = Na_2CO_3 + CO_2 + H_2O$, by the action of dilute sulphuric acid, boiled to

free it from air, on pure sodium carbonate: $Na_2CO_3 + H_2SO_4 = Na_2SO_4 + CO_2 + H_2O$, or by heating a mixture of 1 part of sodium carbonate with 3 parts of potassium dichromate: $Na_2CO_3 + K_2Cr_2O_7 = Na_2CrO_4 + K_2CrO_4 + CO_2$.

Normal carbonates (except those of sodium, potassium, rubidium, caesium, and barium) decompose on heating and evolve carbon dioxide, *e.g.*

$$CaCO_3 \rightleftharpoons CaO + CO_2.$$

Impure carbon dioxide, mixed with nitrogen, is formed by passing a slight excess of air over red-hot charcoal or coke: $C + O_2 = CO_2$. By absorbing the carbon dioxide in concentrated potassium carbonate solution to form a bicarbonate and decomposing this by heat, unmixed carbon dioxide is evolved:

$$K_2CO_3 + CO_2 + H_2O \rightleftharpoons 2KHCO_3.$$

Carbon dioxide from fermentation is also liquefied by compression and sold in steel cylinders. On expanding, the solid ("dry ice") is formed, which is a commercial article (Littler, *J.S.C.I.*, 1932, **52**, 533R), and is sold compressed in 50 lb. blocks or 25 lb. cylinders. Carbon dioxide is a by-product in making hydrogen from water gas (p. 283). Small quantities of snow-like solid CO_2 can be obtained from a cylinder of liquid by tying a flannel bag over the neck and opening the valve with the cylinder horizontal. It can be kept in a Dewar cylinder. The crystal form at $-190°$ is cubic. The liquid cannot exist under atmospheric pressure. The solid mixed with ether or acetone is a convenient cooling agent.

EXPT. 28.—Cut a circular groove in a large cork and fill it with mercury. Place solid carbon dioxide over and wet this with ether. The mercury rapidly freezes.

Carbon dioxide is a heavy colourless gas with a faint pungent smell and slight acid taste. It extinguishes a burning taper, sulphur, phosphorus, etc.; air in which a taper has been burnt to extinction contains $2\frac{1}{2}$ p.c. by volume of carbon dioxide and $17\frac{1}{2}$ p.c. of oxygen. The gas is used in extinguishing fires, preserving fruit (especially apples) and killing insects in grain. Carbon dioxide does not support respiration and animals die in it from suffocation, but it is not poisonous and if oxygen is taken in time recovery with no ill-effect follows.

Burning sodium, potassium, and magnesium continue to burn in carbon dioxide, with separation of pure carbon:

$$4K + 3CO_2 = 2K_2CO_3 + C; \quad CO_2 + 2Mg = 2MgO + C.$$

EXPT. 29.—Burn a piece of magnesium ribbon (or stout wire) in a jar of dry carbon dioxide. Treat the residue with dilute sulphuric acid; magnesia dissolves and black specks of carbon float in the liquid.

A mixture of solid carbon dioxide and magnesium powder burns with a brilliant flash when kindled, leaving magnesia and carbon. A piece of sodium heated in a test-tube of carbon dioxide forms carbon monoxide, which may be kindled: $2Na + 2CO_2 = Na_2CO_3 + CO$. With potassium at 235°, a 17 p.c. yield of oxalate is obtained: $2K + 2CO_2 = K_2C_2O_4$.

Carbon dioxide is a stable gas but at high temperatures it dissociates slightly : $2CO_2 \rightleftharpoons 2CO + O_2$: at 1 atm. pressure the percentage dissociations are :

Temperature abs. -	1000°	1500°	2000°	2500°	3000°
% dissociation -	0·000025	0·0483	2·05	17·6	54·8

Deville (1865) passed a rapid stream of carbon dioxide through a porcelain tube heated to about 1300° C. and collected the issuing gas over alkali solution ; a small amount of carbon monoxide and oxygen was obtained, indicating a dissociation of about 0·2 p.c. The gas is also decomposed by electric sparks (Dixon and Lowe, *J.C.S.*, 1885, **47**, 571), and at 3–5 mm. pressure 65–70 p.c. is decomposed by the silent discharge (Collie, *J.C.S.*, 1901, **79**, 1063).

The *formula* of carbon dioxide is found by burning a piece of dry charcoal in a fixed volume of oxygen. After cooling, the volume of gas is unchanged. Hence 1 vol. of oxygen gives 1 vol. of carbon dioxide, or 1 molecule of oxygen O_2 gives 1 molecule of carbon dioxide, hence the formula is C_xO_2. The density gives the molecular weight 44, and the weight of carbon in this is $44 - 32 = 12$ or 1 atom, hence $x = 1$ and the formula is CO_2.

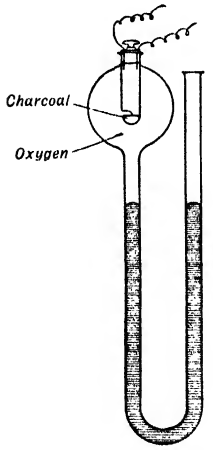


FIG. 224.—The volumetric composition of carbon dioxide.

EXPT. 30.—The apparatus is shown in Fig. 224, the oxygen being confined over mercury. The charcoal is ignited in the spoon by heating it by a spiral of thin platinum wire through which a current is passed.

The *composition by weight* is found by passing a slow stream of pure dry oxygen over a weighed amount of pure charcoal or diamond in a platinum boat strongly heated in a hard glass tube containing a layer of strongly heated copper oxide to oxidise any carbon monoxide formed to carbon dioxide, which is absorbed and weighed in potash bulbs (*College Course*, p. 427). Allowance is made for ash left in the boat, and the weight of carbon combining with 32 parts of oxygen is the atomic weight.

The older results, corrected by Scott (*J.C.S.*, 1897, **71**, 550) for the expansion of the potash solution after absorption of carbon dioxide, which alters the air displacement, are : 11·9938 (Dumas and Stas), 12·0054 (Erdmann and Marchand), 11·9973 (Roscoe), 12·0056 (Friedel), 12·0018 (van der Plaats). Newer values are 12·017 (Scott ; ratio of tetramethylammonium bromide to silver), 12·005 (Richards and Hoover ; ratio of Na_2CO_3 to Ag and to AgBr), 12·003 (Dean ; analysis of silver cyanide and cyanate). The physical method of limiting density gave 12·003 (Leduc ; Rayleigh ; CO), 12·007 (Moles and Salazar ; CO), 12·0039 (Baume and Perrot ; CH_4) and 12·01 (Woodhead and Whytlaw-Gray, *J.C.S.*, 1933, 846 ; CO : p. 15). There are two isotopes, ^{12}C and ^{13}C (p. 188).

Carbonic acid.—Carbon dioxide dissolves in its own volume of water at 15°. At pressures greater than 4–5 atm. at 15° the solubility increases more slowly than the pressure. On lowering the pressure the gas escapes with effervescence

(as from soda-water) but the liquid remains supersaturated. All the gas is expelled on boiling. By compressing the gas to 6½ atm. in presence of water and releasing the pressure a crystalline hydrate $CO_2,6H_2O$ is formed (Villard, 1897). The gas is more soluble in alcohol than in water.

A solution of carbon dioxide in water has a faintly acid taste and turns litmus a port wine red colour, as it is a weak acid. Under pressure the litmus is bright red. Part of the dissolved gas is hydrated to **carbonic acid** H_2CO_3, the dissociation constants of which at 25° are :

$$K_1 = [H^+][HCO_3^-]/[\text{total } CO_2] = 3{\cdot}5 \times 10^{-7},$$
$$K_2 = [H^+][CO_3^{--}]/[HCO_3^-] \quad = 6{\cdot}0 \times 10^{-11}.$$

Carbonic acid HO·CO·OH might be expected to be stronger than formic acid H·CO·OH, since addition of another hydroxyl group should increase the acidic properties. Probably only about 1 p.c. of the dissolved CO_2 is hydrated to carbonic acid, and if the hydrogen ions are referred to the hydrated rather than to the total CO_2 (as above) carbonic acid is twice as strong as formic acid. The hydration reaction $CO_2 + H_2O \rightleftharpoons H_2CO_3$ requires time, and neutralisation with alkali is not instantaneous (McBain, *J.C.S.*, 1912, **101**, 814 ; Mills and Urey, *J.A.C.S.*, 1940, **62**, 1019 ; Olson and Youle, *ibid.*, 1027).

EXPT. 31.—Add 25 c.c. of saturated CO_2 solution diluted to 200 c.c. to 7 c.c. of 0·1*N* NaOH and 5 drops of 1 p.c. phenolphthalein. The red colour *slowly* fades.

The hypothetical *orthocarbonic acid* $C(OH)_4$ is known in esters. Ordinary carbonic acid is dibasic and forms bicarbonates $MHCO_3$ and normal carbonates M_2CO_3. Very weak bases do not form stable carbonates. Normal alkali carbonates are hydrolysed : $CO_3^{--} + H_2O \rightleftharpoons HCO_3^- + OH^-$, *e.g.* 0·1*N* Na_2CO_3 is 3·17 p.c. hydrolysed at 25°.

When carbon dioxide is bubbled through water in contact with amalgamated magnesium it is reduced to formaldehyde (Fenton, *J.C.S.*, 1907, **91**, 687) : $CO_2 + 4H = H{\cdot}COH + H_2O$.

Percarbonates.—On electrolysing a saturated solution of potassium carbonate at −10° to −15° with a platinum anode enclosed in a porous cell, a bluish-white amorphous precipitate of **potassium percarbonate** $K_2C_2O_6$ is deposited at the anode. This may be washed rapidly with cold water, alcohol, and ether, and dried over P_2O_5 (Constam and von Hansen, 1896 ; Brown, *J.A.C.S.*, 1905, **27**, 1222) :

$$\begin{matrix} KO{\cdot}CO{\cdot}OK \\ \\ KO{\cdot}CO{\cdot}OK \end{matrix} = 2K + \begin{matrix} O{\cdot}CO{\cdot}OK \\ | \\ O{\cdot}CO{\cdot}OK \end{matrix}$$

It is fairly stable at room temperature when dry, but is decomposed by water with evolution of oxygen. The sodium salt can be prepared by electrolysis at 0° of a solution of 60 g. of sodium carbonate per lit. (Le Blanc and Zelimann, 1923). By the action of hydrogen peroxide on sodium carbonate a crystalline salt is obtained (Tanatar, 1899 ; Wolffenstein and Peltner, 1908) which was formerly considered to be $Na_2CO_4 + \frac{1}{2}H_2O_2 + H_2O$, but is a carbonate containing hydrogen peroxide of crystallisation : $Na_2CO_3 + 1\frac{1}{2}H_2O_2$.

Electrolytic potassium percarbonate liberates iodine immediately from cold potassium iodide solution, a reaction characteristic of a true percarbonate: $K_2C_2O_6 + 2KI = 2K_2CO_3 + I_2$. The sodium compound $Na_2CO_3,1\frac{1}{2}H_2O_2$ and hydrogen peroxide liberate iodine *slowly*.

By the action of carbon dioxide on a mixture of sodium peroxide and alcohol **sodium percarbonate** $Na_2C_2O_6$ is formed, which combines with sodium peroxide to form **sodium permonocarbonate** Na_2CO_4. Both these salts liberate less iodine than the equivalent of the active oxygen. A second potassium percarbonate $K_2C_2O_6$ prepared by the action of carbon dioxide on alcohol and potassium peroxide resembles the sodium compound and differs from the electrolytic percarbonate in its action on potassium iodide.

Two isomeric percarbonates are thus said to exist:

(α) KO·CO·O·O·CO·OK; (*electrolytic*) (β) KO·O·CO·O·O·CO·OK. (*from peroxide*)

The compound Na_2CO_4 is represented as NaO·O·CO·ONa. The salt $K_2C_2O_6$ (α) is derived from **perdicarbonic** or **percarbonic acid**, and Na_2CO_4 from **permonocarbonic acid**:

By the action of phosphoric acid on potassium percarbonate in ether an unstable solution of percarbonic acid $H_2C_2O_6$ is said to be formed (Bach, 1897). H_2CO_4 is not known.

Carbon Monoxide

Priestley in 1772 obtained a combustible gas (CO) differing from common inflammable air (H_2) and burning with a bright blue flame. Lassone in 1776 obtained it by heating charcoal with zinc oxide and Priestley in 1796 from charcoal and smithy-scales (Fe_3O_4). Cruickshank in 1800 showed that the gas is an oxide of carbon, and in 1801 Clement and Desormes showed that it is formed on passing carbon dioxide over red-hot charcoal and correctly determined its composition by explosion with oxygen to form carbon dioxide. Dalton in 1808 also found that it requires half its volume of oxygen for combustion to carbon dioxide and deduced its formula CO.

Carbon monoxide occurs in small quantities in some volcanic gases. It is formed in the combustion of charcoal or coke in a limited supply of air; the blue flames seen on the top of a clear fire consist of burning carbon monoxide. It is present in burning charcoal fumes, coal gas and automobile exhaust gas, which are very poisonous (Katz and Frevert, *Ind. Eng. Chem.*, 1928, **30**, 31). Traces (up to 31 p.p.m.) are present in gas from a fully aerated Bunsen flame (Davies and Hartley, *J.S.C.I.*, 1927, **46**, 201T) and dangerous amounts are formed by cooled gas flames, as in water heaters, which should have adequate ventilation.

The flickering blue flames of carbon monoxide burning over a clear fire are often supposed to originate in the reduction of carbon dioxide, formed in the lower part of the fire from the entering air, to carbon monoxide in passing

through the mass of incandescent fuel: $C + O_2 = CO_2$ and $CO_2 + C = 2CO$. H. B. Baker (*Phil. Trans.*, 1888, **179**, 571; cf. Dixon, *J.C.S.*, 1899, **75**, 630) thought carbon monoxide is a primary product of the combustion of carbon: $2C + O_2 = 2CO$: he found that carefully dried carbon heated in oxygen dried by prolonged exposure to P_2O_5 reacts only slowly and carbon monoxide is the main product. Rhead and Wheeler (*J.C.S.*, 1910, **97**, 2178; 1911, **99**, 1141; 1912, **101**, 831, 846; 1913, **103**, 461, 1210) state that both carbon monoxide and carbon dioxide are formed simultaneously under these conditions, and think a solid carbon-oxygen complex C_xO_y is first formed, which then breaks up (cf. Armstrong, *J.S.C.I.*, 1905, **24**, 473; Lowry and Hulett, *J.A.C.S.*, 1920, **42**, 1408).

The reduction of carbon dioxide by carbon proceeds somewhat slowly below 800° but above 1000° is fairly rapid. The equilibrium: $C + CO_2 \rightleftharpoons 2CO$, is not usually attained in the combustion of carbon and the composition of the resulting gas is variable. The proportion of CO increases with the temperature. The equilibrium volume percentages at 1 atm. pressure are given in the table.

Temperature °C.	CO_2	CO
850°	6·23	93·77
900°	2·22	97·78
950°	1·32	98·68
1000°	0·59	99·41
1050°	0·37	99·63
1100°	0·15	99·85
1200°	0·06	99·94

Jellinek and Diethelm (*Z. anorg. Chem.*, 1922, **124**, 203) give the formula:

$$\log \frac{p_{CO_2}}{p_{CO}^2} = \log \frac{100x}{(100 - x)^2 p} = \frac{8300}{T} - 1{\cdot}78 \log T + 0{\cdot}000686T - 3{\cdot}876$$

for the equilibrium constant, at 500° to 1100° C. and 1 to 50 atm., where T is the absolute temperature, p_{CO_2}, p_{CO} and p are the partial pressures of CO_2 and CO, and the total pressure, in atm., respectively, and x is the vol. p.c. of CO in the gas.

The reverse reaction: $2CO = CO_2 + C$, was achieved by Deville (1864), who observed the deposition of carbon on a narrow water-cooled silvered copper tube, placed axially in a strongly-heated porcelain tube through which carbon dioxide was passed.

EXPT. 32.—Pass a slow current of carbon dioxide over pieces of charcoal heated to bright redness in a tube (Fig. 225). The carbon dioxide is removed from the gas by soda-lime, and the carbon monoxide burnt at a jet.

Carbon monoxide is formed by passing carbon dioxide over heated zinc dust or iron filings: $CO_2 + Zn = ZnO + CO$, whereas heated alkali metals, magnesium and calcium decompose carbon dioxide with separation of free carbon (p. 475). It is formed by heating charcoal with the oxides of metals which are reduced only at high temperatures, *e.g.* oxides of zinc, iron and manganese:

$ZnO + C = Zn + CO$, whilst oxides of more easily reduced metals, *e.g.* copper, tin and lead, give mostly carbon dioxide. Carbon monoxide is evolved on strongly heating calcium or barium carbonate with charcoal : $BaCO_3 + C = BaO + 2CO$.

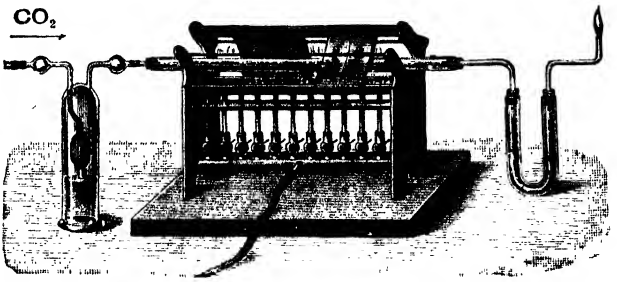


FIG. 225.—Carbon monoxide from carbon dioxide and carbon.

Carbon monoxide is prepared in the laboratory by one or other of three methods all discovered by Döbereiner about 1820, viz. by heating *formic acid* (or sodium formate), *oxalic acid*, or *potassium ferrocyanide* with concentrated sulphuric acid :

$$H{\cdot}COOH = CO + H_2O,$$
$$(COOH)_2 = CO + CO_2 + H_2O,$$
$$HCN + H_2O = CO + NH_3.$$

Formic acid is produced from carbon monoxide and water vapour by the silent discharge : $CO + H_2O = H{\cdot}COOH$, and sodium formate by passing carbon monoxide over heated soda-lime (Berthelot, 1855) : $CO + NaOH = H{\cdot}COONa$.

The gas from formic acid is almost pure : a trace of sulphur dioxide formed by reduction of the sulphuric acid : $CO + H_2SO_4 = CO_2 + SO_2 + H_2O$, is removed by washing with sodium hydroxide solution (Hutton and Petavel, *J.S.C.I.*, 1904, **23**, 87). A mixture of 85 parts of phosphorus pentoxide and 15 parts of water may be used instead of sulphuric acid (Thompson, *Ind. Eng. Chem.*, 1929, **21**, 389).

EXPT. 33.—Concentrated sulphuric acid is heated to 100° in a flask and concentrated formic acid dropped in from a tap-funnel. Cold concentrated sulphuric acid may also be dropped on dry sodium formate. The gas is washed with sodium hydroxide solution. If required dry it is passed over phosphorus pentoxide and collected over mercury.

Note : Carbon monoxide is very poisonous.

Oxalic acid gently heated with concentrated sulphuric acid gives a mixture of equal volumes of carbon monoxide and carbon dioxide (Döbereiner, 1822) : the carbon dioxide is removed by washing with alkali solution.

EXPT. 34.—Cover 25 g. of oxalic acid crystals ($C_2H_2O_4.2H_2O$) in a flask with concentrated sulphuric acid. On heating gently a brisk evolution of gas occurs. This is passed through a wash-bottle containing caustic soda solution and the carbon monoxide collected over water.

Potassium ferrocyanide crystals heated with ten times the weight of concentrated sulphuric acid evolve nearly pure carbon monoxide (Döbereiner, 1820; Fownes, 1843; Adie and Browning, *J.C.S.*, 1900, **77**, 150):

$$K_4Fe(CN)_6 + 6H_2SO_4 + 6H_2O = 2K_2SO_4 + FeSO_4 + 3(NH_4)_2SO_4 + 6CO.$$

The evolution of gas is rather violent and if heating is continued after evolution of CO ceases, much sulphur dioxide is evolved:

$$2FeSO_4 + 2H_2SO_4 = Fe_2(SO_4)_3 + SO_2 + 2H_2O.$$

The carbon monoxide probably comes from formic acid produced by hydrolysis of hydrocyanic acid, the primary product of the action of sulphuric acid on the ferrocyanide (p. 493):

$$HCN + 2H_2O = H{\cdot}COOH + NH_3.$$

Carbon monoxide is a colourless gas with a peculiar *faint* smell (Dixon). It is *very poisonous*; 10 c.c. per kg. weight of an animal produces death, and inhalation of air containing 1 vol. of CO in 800 is fatal in half an hour. Carbon monoxide is not poisonous to green plants or soil bacteria, which oxidise it (Wehmer, 1926), and animals with blood free from haemoglobin can live in an atmosphere of 4 vols. of CO and 1 vol. of O_2.

The poisonous action depends on absorption by the haemoglobin of the blood to form bright-red carboxyhaemoglobin, which is stable and not easily decomposed by oxygen. Oxygen containing 5 p.c. of carbon dioxide should be administered and the patient kept warm. Apparently hopeless cases have been revived by administration of pure oxygen for many hours. In high concentrations of CO collapse occurs almost without warning. Mice and canaries are very susceptible to CO, and are used to detect the gas in mine atmospheres.

The physical properties of carbon monoxide, b.p. $-191{\cdot}5°$, m.p. $-200°$, critical temperature $-138{\cdot}7°$, critical pressure 34·6 atm., are very like those of nitrogen, and the molecular structures are alike:

$$:N:::N: \qquad N\equiv N \qquad :C:::O: \qquad C\overleftarrow{\equiv}O$$

The gas is very stable and may be sparked for a long time without appreciable change if dry. In presence of some heated metals (Pd, Fe, Ni) it is decomposed catalytically: $2CO = C + CO_2$.

Carbon monoxide is sparingly soluble in water, but is readily absorbed by a solution of cuprous chloride in hydrochloric acid, a white crystalline compound $CuCl,CO,2H_2O$ being formed. Ammoniacal cuprous solutions are generally used (Gump and Ernst, *Ind. Eng. Chem.*, 1930, **22**, 382). Water or ammonia must be present; cuprous chloride in dry alcohol does not absorb the gas, but it is absorbed by dry cuprous chloride under pressure to form $CuCl,CO$ (Wagner, 1931). CO is regarded as a neutral oxide but it combines with solid or concentrated alkali on heating, producing formate.

The *composition* of carbon monoxide is determined by passing it over heated copper oxide, the carbon dioxide formed being absorbed in weighed potash bulbs. If the composition of carbon dioxide is assumed, that of carbon

monoxide may then be found. On exploding 2 vols. of the gas with 1 vol. of moist oxygen, 2 vols. of carbon dioxide (absorbable by potash) are formed: $2C_xO_y + O_2 = 2CO_2$. Hence $x = y = 1$, and the formula is CO. This is confirmed by the density.

Many metals form compounds called **carbonyls** with carbon monoxide (p. 875). Carbon monoxide penetrates heated iron and may escape through iron flues of stoves. Carbon monoxide also combines directly with chlorine forming **carbonyl chloride** (*phosgene*) $COCl_2$. It is a reducing agent, liberating many metals from their oxides on heating: $CuO + CO = Cu + CO_2$. Iodine pentoxide is reduced at 90°: $I_2O_5 + 5CO = I_2 + 5CO_2$ (a reaction used for the determination of CO), and a black precipitate of palladium is formed on shaking with palladium chloride solution: $PdCl_2 + H_2O + CO = Pd + CO_2 + 2HCl$.

Carbon monoxide is absorbed in respirators by first passing the air through a drying agent and then through granules of *hopcalite*, a mixture of manganese dioxide and copper oxide (sometimes containing cobaltic oxide Co_2O_3 and silver oxide), which acts as a catalyst for oxidation by atmospheric oxygen (Bray, Lamb and Frazer, *Ind. Eng. Chem.*, 1920, **12**, 213; Lamb and Vail, *J.A.C.S.*, 1925, **47**, 123).

Combustion of carbon monoxide.—Carbon monoxide burns in air or oxygen with a beautiful bright blue flame, which gives a curious impression of silence, and is rather easily extinguished. Carbon dioxide is formed: $2CO + O_2 = 2CO_2$. A mixture of 2 vols. of carbon monoxide and 1 vol. of oxygen explodes when kindled or sparked, but in a small vessel the combustion is not violent.

H. B. Dixon in 1880 found that if the mixed gas is carefully dried by exposure to phosphorus pentoxide it cannot be exploded in a eudiometer, although combination occurs locally in the path of the electric sparks. If a trace of moisture or any gas which contains hydrogen and so produces water on combustion in oxygen (H_2S, NH_3, C_2H_4, HCl, formic acid vapour, but not SO_2, CS_2, C_2N_2) is added, the mixture can be exploded by a spark. M. Traube (1885) found that a burning jet of dry carbon monoxide is extinguished when brought into a vessel of dry air.

EXPT. 35.—Pass a slow stream of carbon monoxide through two sulphuric acid drying towers and a P_2O_5 tube and kindle a small flame at a glass jet. Insert the flame into a 500 c.c. flask in which 50 c.c. of concentrated sulphuric acid has been standing for some hours, uncorking the flask and bringing it horizontally over the flame: this is extinguished. A hydrogen flame continues to burn in the flask.

Girvan (1903) found that 1 molecule of water in 24,000 of gas is still active; the maximum effect is produced by 4·5 p.c. of water vapour. A very dry mixture is exploded by a very powerful spark but only 70–90 p.c. of the carbon monoxide is burnt (Bone and Weston, *Proc. Roy. Soc.*, 1926, **110**, 615).

Several theories have been proposed to explain the effect of moisture on the burning of carbon monoxide (cf. Bone, *J.C.S.*, 1931, 338).

Since carbon monoxide readily reduces steam at high temperatures Dixon supposed that the reaction $CO + H_2O \rightleftharpoons CO_2 + H_2$ first occurs, and the hydrogen then burns to reproduce water, which thus enters into a cycle of changes.

Traube (1885) supposed that hydrogen peroxide is an intermediate product:

$$CO + \begin{matrix}OHH\\OHH\end{matrix} + O_2 = CO\begin{matrix}OH\\OH\end{matrix} + H_2O_2$$

$$H_2O_2 + CO = CO\begin{matrix}OH\\OH\end{matrix}$$

$$CO\begin{matrix}OH\\OH\end{matrix} = CO_2 + H_2O,$$

but von Wartenberg and Sieg (*Ber.*, 1920, **53**, 2192), who confirmed the presence of free hydrogen in a flame of moist carbon monoxide, showed that hydrogen peroxide is probably formed by a secondary reaction. They detected formic acid by playing the flame on ice.

Another theory (Bonhoeffer and Haber, *Z. phys. Chem.*, 1928, **137**, 263; cf. Jackson, *J.A.C.S.*, 1935, **57**, 82) postulates a chain reaction involving atomic hydrogen and hydroxyl radicals:

$$H + O_2 + CO = HO + CO_2$$
$$HO + CO = CO_2 + H.$$

Catalytic effects of moisture.—Numerous cases of the catalytic effect of moisture are known (Mellor and Russell, *J.C.S.*, 1902, **81**, 1272). Dry chlorine does not combine with many dry metals, except mercury. Dry carbon monoxide and oxygen do not explode on sparking. After prolonged drying over phosphorus pentoxide, carbon combines only slowly with oxygen on heating; ammonium chloride and calomel volatilise on heating without dissociation; ammonia and hydrogen chloride do not combine on mixing; and sulphur and phosphorus may be distilled unchanged in oxygen. Nitrogen trioxide after prolonged drying in the liquid state over P_2O_5 volatilises as N_4O_6, but in presence of a minute trace of moisture this instantly dissociates into NO and NO_2. The boiling point of liquid N_4O_6 is raised from $-2°$ to $+43°$ by drying for three years. Calomel dried for six months over P_2O_5 at 115° will not vaporise at all at 352°, when its usual vapour pressure is 347 mm. Nitric oxide and oxygen, hydrogen and chlorine, and ammonia and carbon dioxide, do not react when very pure and dry. Sodium and potassium scarcely react with dry oxygen, although dry boron, tellurium, arsenic and antimony react readily under the usual conditions (H. B. Baker, *J.C.S.*, 1894, **65**, 611, 623; some findings are disputed by later workers, but the technique is difficult).

In some cases the presence of *pure* water is not sufficient to catalyse a reaction, but a trace of impurity is needed. H. B. Baker (*J.C.S.*, 1902, **84**, 400; confirmed by Bone and Andrew, *ibid.*, 1906, **89**, 652) found that a mixture of very pure hydrogen and oxygen sealed in glass tubes over purified P_2O_5 did not combine after prolonged drying when the tube was heated with a flame or if a spiral of silver wire was heated almost to the melting point in the gas; with less prolonged drying the gases combined slowly, *but no explosion occurred.* The water produced by the combination was, according to H. E. Armstrong's theory (*J.C.S.*,

1886, **49**, 112; 1903, **83**, 1088), too pure to form an electrically-conducting circuit, which he considered necessary for chemical change:

Before		After	
CO | O H_2 | O		CO_2 | H_2O	
CO | O H_2 | O		CO_2 | H_2O	

The water normally forms a "closed conducting circuit" owing to traces of impurity, and the oxygen acts as a depolariser.

Producer gas.—When air is passed through a mass of incandescent coke a mixture of nitrogen and carbon monoxide, with some carbon dioxide, and some sulphur dioxide from sulphur compounds in the coke, is formed. This is called *producer gas* (or *air gas*). Some steam is usually mixed with the air and the gas then contains some hydrogen and a little methane:

CO 26 N_2 49 CO_2 6 H_2 18·7 CH_4 0·3 vol. p.c.

The reactions in the formation of producer gas are exothermic:

$$2C + O_2 = 2CO + 54 \text{ k. cal.}$$
$$C + O_2 = CO_2 + 94 \text{ k. cal.},$$

so that the reaction goes on without interruption. The ratio CO/CO_2 in the gas increases with temperature (p. 479).

Producer gas is made in closed gas-producers lined with firebricks, in which the coke rests on a grate below which the air is admitted. The hot gas may be burnt directly in a furnace by admitting the proper amount of "secondary" air. If coal is used instead of coke the draught through the producer is downwards, when the coal gas is decomposed by the incandescent fuel.

Water gas.—When steam is blown through incandescent coke a mixture of carbon monoxide, carbon dioxide and hydrogen is formed, known as *water gas*:

$$C + 2H_2O = CO_2 + 2H_2 - 17 \text{ k. cal. } (\textit{dull}\text{-red heat}),$$
$$C + H_2O = CO + H_2 - 28 \text{ k. cal. } (\textit{bright}\text{-red heat}).$$

Both reactions occur, since in presence of steam the carbon monoxide is partly converted into dioxide by the "water gas" reaction: $CO + H_2O \rightleftharpoons CO_2 + H_2$.

The proportion of carbon monoxide increases as the temperature rises, as is seen from the following table giving the results of Bunte:

Temp.	Percentage of steam decomposed	Composition of gas by volume			$\frac{CO}{CO_2}$	$\frac{H_2}{CO}$	$\frac{CO}{CO+CO_2}$
		H_2	CO	CO_2			
675°	8·8	65·2	4·9	29·8	0·16	13·3	0·141
758	25·3	65·2	7·8	27·0	0·29	8·4	0·224
840	41·0	61·9	15·1	22·9	0·65	4·1	0·397
955	70·2	53·3	39·3	6·8	5·80	1·35	0·853
1010	94·0	48·8	49·7	1·5	33·10	0·98	0·972
1060	98·0	50·7	48·0	1·3	36·8	1·05	0·975
1125	99·4	50·9	48·5	0·6	80·8	1·05	0·988

A typical water gas contains :

H_2 52 CO 40 CO_2 4·5 N_2 2·1 CH_4 0·8 H_2S 0·6 vol. p.c.

The hydrogen sulphide is formed from sulphur compounds in the coke. Average water gas has a calorific value of 350 B.Th.U. per cu. ft. As it requires only 2·5 vols. of air for complete combustion it gives a hot flame.

The water gas reactions absorb heat and the red-hot coke gradually cools, the carbon dioxide in the gas thus increasing. After a time (say 8 mins.) the steam is shut off and air blown through for a short time (say 2 mins.) to raise the temperature of the fuel to bright redness, the gas formed being turned to waste. To keep the temperature uniform, the steam is blown alternately upwards and downwards through the gas-producer.

Semi-water gas is made by passing a mixture of steam and air *continuously* through red-hot coke, the heat evolved by the combustion of the carbon with the oxygen of the air maintaining the temperature for the water gas reaction with the steam. **Mond gas** is formed with a large excess of steam which keeps the temperature low (650°), and allows of the recovery as ammonia of a large part of the nitrogen of the coal-slack used.

Carburetted (" enriched ") **water gas** is formed by mixing water gas with hydrocarbons, partly unsaturated, which burn with a luminous flame. Water gas alone burns with a blue non-luminous flame but may be used with Welsbach mantles for illuminating purposes.

In the manufacture of carburetted water gas two towers packed with chequer-brickwork are placed after the producer (Fig. 226). The first, called the car

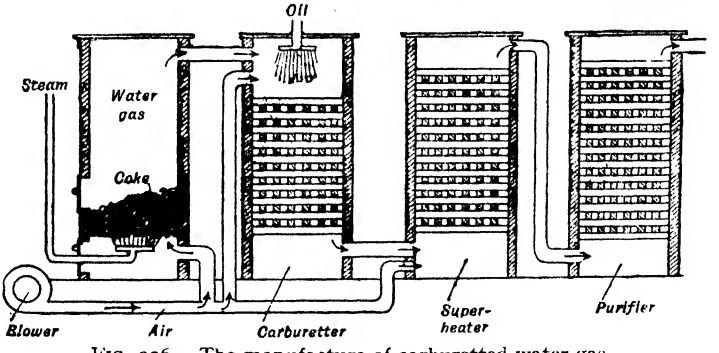


FIG. 226.—The manufacture of carburetted water gas.

buretter, and the second, called the **superheater,** are first heated to redness by hot producer gas from the air-blow passing down the first, mixing with air, and burning in the second. The water gas from the steam-blow is now passed through the towers and a spray of mineral oil is injected into the carburetter. This vaporises and the mixture of water gas and oil vapour passes through the red-hot bricks in the superheater, where the oil vapour is decomposed or " cracked," and a permanent gas rich in ethylene, which burns with a luminous flame, is

formed. The gas is passed through a purifier, in which hydrogen sulphide (from sulphur in the coke) is taken out by iron oxide. **Pintsch gas** is formed by spraying oil into hot retorts and passing the gas through a condenser, scrubber, and lime purifier.

The composition of a typical carburetted water gas in vol. p.c. is :

H_2	40	N_2	6·8	saturated hydrocarbons	16
CO	30	O_2	0·2	unsaturated hydrocarbons	7

The calorific value of producer and semi-water gas is low, being usually about 125 B.Th.U. per cu. ft., as compared with about 600 for good coal gas and 350 for water gas.

Carbonyl Compounds

Carbon monoxide CO is unsaturated and combines directly with halogens (except iodine), oxygen, and sulphur, to form *carbonyl halides* COX_2, *carbon dioxide*, and *carbonyl sulphide* COS, in which CO functions as a bivalent radical. These compounds may also be regarded as derivates of (the hypothetical) carbonic acid $CO(OH)_2$. The *metal carbonyls* (p. 875) form a different group of compounds.

Carbonyl fluoride COF_2, colourless gas, m.p. −114°, b.p. −83°.
Carbonyl chloride $COCl_2$, colourless gas, m.p. −118°, b.p. 8·2°.
Carbonyl bromide $COBr_2$, colourless liquid, b.p. 64·5°.
Carbonyl sulphide COS, colourless gas, m.p. −138·2°, b.p. −50·2°.

Carbon monoxide also combines with cyanogen when exposed to light to form solid **carbonyl cyanide** $CO(CN)_2$.

Carbonyl fluoride COF_2 is a gas formed by the explosive reaction of carbon monoxide and fluorine on sparking, by burning fluorine in an atmosphere of carbon monoxide, and by the action of carbon monoxide on silver difluoride (Ruff and Miltschitzky, 1934) : $2AgF_2 + CO = 2AgF + COF_2$. It reacts with water, glass and many metals, but not mercury and silver.

Carbonyl chloride $COCl_2$ is formed when a mixture of equal volumes of carbon monoxide and chlorine is exposed to bright sunlight (J. Davy, 1812)—hence its name *phosgene* (Greek *phos*, light, and *gennao*, I produce)—or is passed over active charcoal (Paternò, 1878 ; Pope, etc., *J.C.S.*, 1920, **117**, 1410 ; *Ind. Eng. Chem.*, 1919, **11**, 263 ; Jacqué, *Chim. et Ind.*, 1928, **19**, 24T) : $CO + Cl_2 = COCl_2$. It is also formed by dropping fuming sulphuric acid into boiling carbon tetrachloride : $CCl_4 + 2SO_3 = COCl_2 + S_2O_5Cl_2$, disulphuryl chloride being a by-product (Schützenberger, 1869).

Carbonyl chloride is a colourless gas with a penetrating suffocating smell and is poisonous. It is easily liquefied, b.p. 8·2°. It does not fume in moist air but is easily hydrolysed by water : $COCl_2 + H_2O = CO_2 + 2HCl$. With ammonia gas it forms urea, the diamide of carbonic acid : $COCl_2 + 4NH_3 = CO(NH_2)_2 + 2NH_4Cl$.

The amide of carbonic acid, $HO{\cdot}CO{\cdot}NH_2$, is **carbamic acid**. Its ammonium salt $NH_4O{\cdot}CO{\cdot}NH_2$ is contained, with ammonium bicarbonate NH_4HCO_3, in commercial " carbonate of ammonia " (p. 319).

Carbonyl bromide $COBr_2$ is slowly formed by the action of light on a mixture of carbon monoxide and bromine vapour, but is best prepared by dropping concentrated sulphuric acid into carbon tetrabromide at 160°:

$$CBr_4 + H_2SO_4 = COBr_2 + SO_3 + 2HBr.$$

Carbonyl sulphide (or *carbon oxysulphide*) COS, discovered by Than (1867), is a gas formed when a mixture of carbon monoxide and sulphur vapour is passed through a heated tube: $2CO + S_2 \rightleftharpoons 2COS$, when sulphur dioxide is passed over red-hot charcoal: $3C + 2SO_2 = 2COS + CO_2$, and by the action of sulphur trioxide on carbon disulphide: $3SO_3 + CS_2 = COS + 4SO_2$. The most convenient method of preparation is by the action of warm diluted sulphuric acid (5 vols. of H_2SO_4 to 4 vols. of water) on ammonium thiocyanate, when the unstable thiocyanic acid first formed is hydrolysed: $HCNS + H_2O = COS + NH_3$, the ammonia combining with the sulphuric acid.

The gas contains hydrocyanic acid and carbon disulphide vapour as impurities. The hydrocyanic acid is removed by passing through *concentrated* sodium hydroxide solution, the carbon disulphide vapour by passing through concentrated sulphuric acid, followed by a mixture of trimethyl phosphine $P(CH_3)_3$, pyridine and nitrobenzene, or through sodium azide NaN_3 solution. The gas may be collected and stored over concentrated sulphuric acid.

Pure carbonyl sulphide is prepared by passing the crude gas into alcoholic potash and decomposing the potassium ethyl thiocarbonate (*Bender's salt*), which separates, with dilute hydrochloric acid:

$$C_2H_5O{\cdot}CS{\cdot}OK + HCl = COS + C_2H_5OH + KCl,$$

or by decomposing ammonium thiocarbamate with dilute hydrochloric acid (Stock and Kuss, *Ber.*, 1917, **50**, 159):

$$NH_4{\cdot}S{\cdot}CO{\cdot}NH_2 + 2HCl = COS + 2NH_4Cl.$$

Carbonyl sulphide is a colourless gas, odourless when pure and with anaesthetic properties, which liquefies at 0° under 12·5 atm. pressure. The molecule O=C=S is linear. The gas is moderately soluble in water and readily in toluene. The aqueous solution is slowly hydrolysed (Thompson, Kearton and Lamb, *J.C.S.*, 1935, 1033): $COS + H_2O = CO_2 + H_2S$, but small quantities of carbonyl sulphide are said to be present in the mineral waters of Harkány and Parád in Hungary. It is absorbed and hydrolysed by *dilute* alkali: $COS + 4OH' = CO_3'' + S'' + 2H_2O$.

Carbonyl sulphide is decomposed by a heated platinum spiral without change of volume into sulphur and carbon monoxide: $COS = CO + S$; in contact with hot glass or quartz the reaction $2COS = CS_2 + CO_2$ occurs.

Carbonyl sulphide is very inflammable, a glowing chip igniting it, and burns with a blue slightly luminous flame; the mixture with oxygen explodes feebly when sparked: $2COS + 3O_2 = 2CO_2 + 2SO_2$; the mixture when dried by P_2O_5 does not always explode (Russell, *J.C.S.*, 1900, **77**, 361).

Carbonyl selenide COSe, b.p. −22·9°/725 mm., m.p. −122° (Pearson and Robinson, *J.C.S.*, 1932, 652), is formed by passing carbon monoxide over heated selenium.

Carbon suboxide C_3O_2, the second anhydride of malonic acid, is formed as a gas when this or (better) ethyl malonate is heated with a large excess of phosphorus pentoxide at 300° under 12 mm. pressure (Diels and Wolf, 1906):

$$CH_2(COOH)_2 = C_3O_2 + 2H_2O$$
$$CH_2(COOC_2H_5)_2 = C_3O_2 + 2H_2O + 2C_2H_4;$$

also when fused diacetyltartaric anhydride is passed through a tube at 650° (Ott and Schmidt, 1922; Hurd and Pilgrim, *J.A.C.S.*, 1933, **55**, 757; Reyerson and Kobe, *Chem. Rev.*, 1930, **7**, 479):

$$\begin{matrix} CH_3{\cdot}COO{\cdot}CH{-}CO \\ \quad\quad\quad\quad\quad | \\ CH_3{\cdot}COO{\cdot}CH{-}CO \end{matrix}\!\!>\!O = 2CH_3COOH + CO + C_3O_2.$$

Both reactions indicate the structure O=C=C=C=O, which is confirmed by the reactions of C_3O_2. The gas is liquefied by cooling and purified by fractionation, b.p. 6°, m.p. −111·3°.

Carbon suboxide is a colourless pungent-smelling poisonous gas. It decomposes rapidly on heating or in contact with phosphorus pentoxide, giving CO, CO_2 and red solid polymers; the liquid slowly polymerises at room temperature.

According to Klemenc (1934–7) carbon suboxide at 200° forms carmine-red **dicarbon gas**: $C_3O_2 = CO_2 + C_2$, which quickly forms solid carbon. The C_3O_2 prepared from malonic acid is supposed to contain some C_5O_2.

Carbon suboxide gas burns in air with a blue-edged smoky luminous flame, and the mixture with oxygen explodes when sparked: $C_3O_2 + 2O_2 = 3CO_2$. Carbon suboxide dissolves in benzene, xylene and carbon disulphide, and readily in water to form malonic acid. It reacts with sulphur dioxide at low temperatures: $O{:}C{:}C{:}C{:}O + SO_2 = CO_2 + OC{:}C{:}SO$.

Carbon Sulphides

Three sulphides of carbon are known, **carbon disulphide** CS_2, **monosulphide** $(CS)_x$, and **subsulphide** C_3S_2, corresponding with the three oxides. The disulphide forms with alkali sulphides the **thiocarbonates**, analogous to the carbonates: $CS_2 + Na_2S = Na_2CS_3$ (cf. $CO_2 + Na_2O = Na_2CO_3$).

Carbon disulphide CS_2 was discovered by Lampadius in 1796 by distilling charcoal with iron pyrites. It is prepared by passing sulphur vapour over red-hot carbon (Clement and Desormes, 1802). From solid sulphur the reaction is endothermic: $[C] + 2[S] = CS_2 - 19$ k. cal., but with gaseous sulphur in the form S_2 (at 850°) it is exothermic and reversible (Koref, 1910): $[C] + (S_2) = CS_2 + 12{\cdot}5$ k. cal.

In the modern (Zahn's) process of manufacture the sulphur is fused and is converted into vapour in a pre-heater *A* (Fig. 227) which is cast integral with the oval iron retort *B* containing charcoal and heated at 850°–900° by gas. Both are lined with refractory bricks. The carbon disulphide vapour is con-

densed by good cooling and the liquid purified by careful fractional distillation. It may be further purified by distillation over lead acetate, or by shaking with mercury until it no longer blackens it, and then distilling first over white wax and then over phosphorus pentoxide.

In Taylor's process (1899 ; *Ind. Eng. Chem.*, 1912, **4**, 557), used in America, electrical heating by carbon arcs in a mass of pieces of charcoal or coke is used, melted sulphur being run in below (Fig. 228). The sulphur vapour rises through

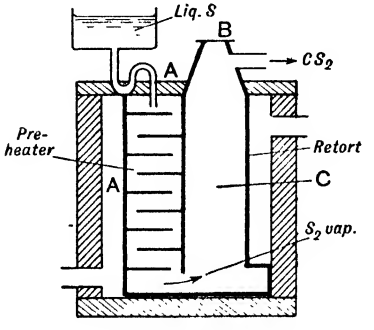


FIG. 227.—Carbon disulphide retort.

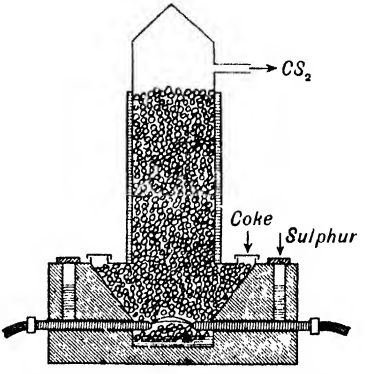


FIG. 228.—Taylor's carbon disulphide furnace.

the long column of heated carbon and the carbon disulphide vapour taken off at the top is condensed.

Carbon disulphide is a colourless mobile liquid of high refractive index which is very volatile, b p. 46·25°, m.p. −112·8° (the solid is tetragonal), s. g. at 0° 1·2923, at 20° 1·2661 ; it is almost insoluble in water (100 c.c. dissolve 0·204 g. of CS_2 at 0°, 0·179 at 20°, and 0·014 at 49°). It mixes with absolute alcohol, ether and oils, dissolves sulphur, white phosphorus, indiarubber, camphor, resins, etc., and is used as a solvent. Carbon disulphide has usually an unpleasant odour which is removed by careful purification, when the liquid smells of chloroform, but the smell soon becomes unpleasant again. The vapour has a low ignition temperature (about 200° in air) : a test-tube filled with hot oil, or a heated tripod stand, inflames the vapour. A mixture of the vapour with air or oxygen explodes when kindled or sparked, even if quite dry (Baker, *J.C.S.*, 1894, **65**, 611 ; Dixon and Russell, *J.C.S.*, 1899, **75**, 600), the most violent explosion occurring with $2CS_2 + 5O_2 = 2CO + 4SO_2$. Some SO_3 and CO_2 are also formed but no free carbon is deposited. If a little mercury fulminate is exploded in a tube filled with carbon disulphide vapour, decomposition commences with separation of sulphur and carbon, but is not propagated through the vapour.

The vapour is decomposed by heated potassium : $CS_2 + 4K = 2K_2S + C$. When chlorine is passed into boiling carbon disulphide containing a little iodine, carbon tetrachloride is formed :

$$CS_2 + 3Cl_2 = CCl_4 \text{ (b.p. 77°)} + S_2Cl_2 \text{ (b.p. 138°)}.$$

Carbon disulphide vapour is a powerful poison: it is used to kill moths in furs, etc., and mice and rats in grain elevators. Carbon disulphide is now mostly used to make viscose (artificial silk) by the xanthate process and in the cold vulcanisation of rubber: it is not now much used as a solvent, being replaced by trichlorethylene. Sodium xanthate S=C(OEt)SNa, made by dissolving carbon disulphide in alcoholic sodium hydroxide, is used in ore flotation. Viscose is the sodium salt of cellulose xanthate.

A mixture of carbon disulphide vapour and hydrogen passed over heated nickel at 450° yields hydrogen sulphide: $CS_2 + 2H_2 = C + 2H_2S$. When the vapour is passed over red-hot copper, carbon and cuprous sulphide are formed: $CS_2 + 4Cu = C + 2Cu_2S$. A mixture of the vapour with hydrogen sulphide or steam when passed over red-hot copper gives methane (Berthelot, 1856–8):

$$CS_2 + 2H_2S + 8Cu = 4Cu_2S + CH_4$$
$$CS_2 + 2H_2O + 6Cu = 2Cu_2S + 2CuO + CH_4.$$

Carbon disulphide reacts with a solution of triethyl phosphine $P(C_2H_5)_3$ in ether, forming a red crystalline compound $P(C_2H_5)_3,CS_2$.

Thiocarbonic acid.—Carbon disulphide CS_2 behaves towards alkali sulphides as a *thicanhydride*, forming salts of *thiocarbonic acid*, the reaction being analogous to the formation of a carbonate from carbon dioxide and an alkali oxide (Berzelius, 1826):

$$CS_2 + Na_2S = Na_2CS_3; \quad \text{cf. } CO_2 + Na_2O = Na_2CO_3.$$

Carbon disulphide dissolves in alkali sulphide solution; it reacts more slowly when shaken with alkali hydroxide solution, when a carbonate is also formed:

$$3CS_2 + 6NaOH = 2Na_2CS_3 + Na_2CO_3 + 3H_2O.$$

Pure **sodium thiocarbonate** Na_2CS_3,H_2O separates in pinkish-yellow crystals on adding ether to a solution of carbon disulphide in alcoholic NaHS solution (Yeoman, *J.C.S.*, 1921, **119**, 38): $2NaHS + CS_2 = Na_2CS_3 + H_2S$.

A deep red solution and orange-yellow crystals of **ammonium thiocarbonate** $(NH_4)_2CS_3$ are formed when carbon disulphide and concentrated ammonia stand together for a few days, or by prolonged refluxing of carbon disulphide with ammonium pentasulphide solution; yellow crystals of **ammonium thiopercarbonate** $(NH_4)_2CS_4$ are formed by less prolonged action: both salts are purified by washing with carbon disulphide and ether.

By adding ammonium thiocarbonate crystals to a large excess of concentrated hydrochloric acid, free **thiocarbonic acid** H_2CS_3 separates as a bright red liquid. By adding ammonium thiopercarbonate to 98 p.c. formic acid, **thiopercarbonic acid** H_2CS_4, not quite pure, separates: with hydrochloric acid only H_2CS_3 and sulphur are formed (Mills and Robinson, *J.C.S.*, 1928, 2326). H_2CS_4 can be dried by P_2O_5: on distillation it decomposes: $H_2CS_4 = H_2S_2 + CS_2$.

In destroying *Phylloxera*, a kind of aphid infesting vines, the vines are sprayed with a solution of sodium thiocarbonate, which is slowly decomposed by atmospheric carbon dioxide with liberation of carbon disulphide: $Na_2CS_3 + CO_2 + H_2O = Na_2CO_3 + CS_2 + H_2S$.

Thiocarbonates give a brown precipitate of $CuCS_3$ with copper salts, a red precipitate of $PbCS_3$ with lead salts, and a yellow precipitate of Ag_2CS_3 with dilute silver nitrate. These rapidly become black from formation of sulphides. Ferric salts give an intense red colour.

Carbon subsulphide C_3S_2 (corresponding with C_3O_2) is formed by striking an arc under carbon disulphide with a carbon cathode and an anode of zinc, or antimony containing 7 p.c. of carbon (Lengyel, 1893; Stock and Praetorius, 1912): $3CS_2 + 4Zn = C_3S_2 + 4ZnS$. The liquid is distilled in vacuum and the vapour condensed at $-40°$, when yellowish-red solid C_3S_2, m.p. $-0·5°$, is formed. The structure is S:C:C:C:S. The vapour has an offensive smell and produces a copious flow of tears. A bromide $C_3S_2Br_6$, formed directly, has a not unpleasant aromatic smell.

A brown solid polymerised **carbon monosulphide** $(CS)_x$ is formed when carbon disulphide is exposed to light, and by the action of nickel carbonyl on thiocarbonyl chloride at room temperature (Dewar and Jones, *J.C.S.*, 1910, **97**, 1226): $Ni(CO)_4 + CSCl_2 = NiCl_2 + 4CO + CS$. A gaseous non-polymerised form is said to be produced on passing CS_2 vapour at low pressure through an ozoniser. Carbon monosulphide and ozone are formed during the pre-flame combustion of carbon disulphide vapour (Dixon, *Rec. Trav. Chim.*, 1925, **44**, 305; Griffith and Hill, *J.C.S.*, 1938, 2037).

Carbon sulphoselenide CSSe and **sulphotelluride** CSTe are prepared by striking an arc under carbon disulphide between a graphite cathode and an anode of graphite and selenium, or tellurium, respectively. They are yellow and red liquids, respectively (Stock, etc., 1914; Briscoe, etc., *J.C.S.*, 1929, 56).

Thiocarbonyl chloride (*thiophosgene*) $CSCl_2$ (Kolbe, 1843), best prepared by reducing thiocarbonyl perchloride (see below) with tin and hydrochloric acid, is a red mobile fuming liquid, b.p. 73·5°, s. g. 1·51, with a most offensive smell.

Thiocarbonyl perchloride $CSCl_4$ or $Cl_3C{\cdot}SCl$ (Rathke, 1873) is best prepared by passing dry chlorine into carbon disulphide containing a little iodine at 20°–25°: $2CS_2 + 5Cl_2 = 2CSCl_4 + S_2Cl_2$, running into hot water, distilling in steam, drying over calcium chloride, and fractionating. It is a yellow liquid, b.p. 140°, s. g. 1·71, with a very disagreeable lachrymatory odour (Frankland, etc., *J.S.C.I.*, 1920, **39**, 256, 313T).

Cyanogen

Cyanogen is evolved on heating dry silver, mercury, or gold cyanide, the most convenient being mercuric cyanide, which is heated to dull redness in a hard glass or steel tube (Gay-Lussac, 1815): $Hg(CN)_2 = Hg + C_2N_2$. A heavy brown powder called *paracyanogen* produced at the same time is probably a polymer $(CN)_n$, as it decomposes slowly into cyanogen at 800°. The gas is evolved at a lower temperature if mercuric chloride is mixed with the cyanide: $Hg(CN)_2 + HgCl_2 = Hg_2Cl_2 + C_2N_2$.

Expt. 36.—Heat a little mercuric cyanide in a hard glass tube fitted with a rubber stopper and hard glass or metal jet. Kindle the gas at the jet; it burns with a peach-blossom coloured flame. *N.B.—Cyanogen is very poisonous.*

Less pure cyanogen (containing some carbon dioxide and hydrocyanic acid) is prepared (Jacquemin, 1885) by dropping concentrated potassium or sodium

cyanide solution into a warm solution of 1 pt. of copper sulphate crystals in 2 pts. of water. A yellow precipitate of cupric cyanide $Cu(CN)_2$ first formed quickly decomposes into cyanogen gas and white cuprous cyanide :

$$2Cu^{\cdot\cdot} + 4CN' = 2Cu(CN) + C_2N_2.$$

By warming the cuprous cyanide with ferric chloride solution the rest of the cyanogen is evolved :

$$2Cu(CN) + 2FeCl_3 = 2CuCl + 2FeCl_2 + C_2N_2.$$

Hydrocyanic acid vapour is removed by passing the gas over cotton-wool soaked in silver sulphate solution.

Cyanogen is a colourless gas, soluble in water ($4\frac{1}{2}$ vols. in 1 vol. H_2O at 20°), and must be collected over mercury. It has a smell of bitter almonds and is *very poisonous*. When cooled it condenses to a colourless liquid, b.p. −20·7°, which freezes below −35° to a white solid, m.p. −27·92°. The density of the gas corresponds with the formula C_2N_2. Cyanogen is endothermic : $2C$ (graphite) $+ N_2 = C_2N_2 - 70$ k. cal.

Cyanogen is absorbed by alkali hydroxide solution, forming a mixture of cyanide and cyanate (cf. Cl_2) :

$$C_2N_2 + 2OH' = CN' + CNO' + H_2O.$$

With water at 0° hydrocyanic and cyanic acids are formed :

$$C_2N_2 + H_2O = HCN + HCNO.$$

A mixture of equal volumes of cyanogen and oxygen is exploded by an electric spark, even when carefully dried over phosphorus pentoxide, forming carbon monoxide and nitrogen : $C_2N_2 + O_2 = 2CO + N_2$; with double the volume of oxygen, the monoxide is burnt to carbon dioxide (Dixon, *Phil. Trans.*, 1903, **200**, 315). When a *dry* cyanogen and oxygen mixture is burnt in a Smithells apparatus (p. 471), the *dry* CO formed will burn in dry air if kindled just above the first flame.

The structure of cyanogen N≡C·C—≡N is shown by its reduction to ethylenediamine $H_2N{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2$.

Hydrocyanic acid.—When potassium cyanide is distilled with a mixture of equal volumes of sulphuric acid and water, the vapour of hydrocyanic acid is evolved (Wade and Panting, *J.C.S.*, 1898, **73**, 255) :

$$KCN + H_2SO_4 = KHSO_4 + HCN.$$

(With *concentrated* sulphuric acid, carbon monoxide is formed in large quantities : $HCN + 2H_2O = H{\cdot}COOH + NH_3 = H_2O + CO + NH_3$). The gas is dried by a U-tube of calcium chloride and liquefied in a tube cooled in ice and salt. It is purified by distillation over P_2O_5 (Nef, *Annalen*, 1895, **287**, 265 ; Gattermann, *ibid.*, 1907, **357**, 318). A convenient method of preparation (Partington and Carroll, *Phil. Mag.*, 1925, **49**, 665) is to pass pure dry hydrogen sulphide slowly over dry mercuric cyanide at 30° in a long glass tube and condense in a freezing mixture : $Hg(CN)_2 + H_2S = HgS + 2HCN$.

Hydrocyanic acid is formed when a mixture of acetylene and nitrogen is sparked: $C_2H_2 + N_2 = 2HCN$; when a mixture of nitrogen, hydrogen and methane is passed through a carbon arc: $2CH_4 + N_2 = 2HCN + 3H_2$; and (as Scheele found) by passing ammonia over strongly heated charcoal (Badger, *J.A.C.S.*, 1924, **46**, 2166): $NH_3 + C \rightleftharpoons HCN + H_2$.

Anhydrous hydrocyanic acid is a colourless liquid, b.p. 25·65°, m.p. −15°. The vapour burns with a purple flame in air, and the mixture with oxygen can be exploded in a eudiometer:

$$4HCN + 5O_2 = 2H_2O + 2N_2 + 4CO_2.$$

It is *a very dangerous poison* (0·06–0·07 g. is fatal) and its preparation and use require the most stringent precautions. It is used in fumigation for killing insects and vermin (Carlisle, *Ind. Eng Chem.*, 1933, **25**, 959).

A solution of hydrocyanic acid is prepared by distilling potassium ferrocyanide with diluted sulphuric acid (1 : 2):

$$2K_4Fe(CN)_6 + 3H_2SO_4 = 3K_2SO_4 + K_2Fe[Fe(CN)_6] + 6HCN.$$

When diluted to $2\frac{1}{2}$ p.c. HCN it is called *prussic acid*, and is very poisonous: it is used, highly diluted, in remedies for bronchial catarrh, etc.

The smell of bruised fruit kernels, laurel leaves and moist bitter almonds is due to hydrocyanic acid (some persons cannot detect the smell), and it is curious that Scheele, who discovered hydrocyanic acid (1782), did not know it was poisonous: this was first suspected from its formation from the poisonous bitter almonds by distillation with water. Ammonia or chlorine water is used as an antidote, but larger doses are almost instantaneously fatal. The best antidote is said to be ferrous hydroxide, obtained by adding 1·5 g. of caustic soda in 300 c.c. of water and 2 g. of magnesia to 7·5 g. of ferrous sulphate crystals in 300 c.c. of water.

Hydrocyanic acid is very weak: $K = [H^{\cdot}][CN'] / [HCN] = 1{\cdot}3 \times 10^{-9}$ at 18°, and alkali cyanides are hydrolysed in solution: $CN' + H_2O \rightleftharpoons HCN + OH'$; at 25° $K = [HCN][OH'] / [CN'] = 2{\cdot}5 \times 10^{-5}$ (Harman and Worley, 1925).

Although organic derivatives with structures R°C : ⋮ N :, R—C ≡ N (cyanides), and R ° N ⋮⋮ : C :, R—N ⇉ C (isocyanides) are isomeric, the cyanide ion from the two corresponding acids is identical, [: N : : : C :]′.

Chlorine passed into aqueous hydrocyanic acid forms gaseous **cyanogen chloride** CN·Cl, which condenses in a freezing mixture to a colourless mobile liquid, b.p. 12·7° (Berthollet, 1787). The liquid if slightly acidified rapidly polymerises to white solid **cyanuric chloride** $(CNCl)_3$. Cyanogen chloride reacts with alkalis forming chloride and cyanate: $CN{\cdot}Cl + 2KOH = KCl + KCNO + H_2O$. It is the chloride of cyanic acid, HCNO. With ammonia it forms **cyanamide** $CN{\cdot}NH_2$.

Cyanogen chloride is best prepared by acting on sodium cyanide, a little water, and carbon tetrachloride, with chlorine gas and distilling. It is used in place of hydrocyanic acid for fumigation, since it is lachrymatory and is easily detected.

Bromide reacts with hydrocyanic acid or potassium cyanide to form **cyanogen bromide** CN·Br, and iodine with potassium or mercuric cyanide to form **cyanogen iodide**

CN·I : both are colourless crystalline solids. **Cyanogen fluoride** CN·F is a colourless gas, insoluble in water, formed by the reaction : $CN{\cdot}I + AgF = CN{\cdot}F + AgI$ at 270° (Cosslett, 1931). All the halogen compounds of cyanogen are very poisonous.

The alkali cyanides are formed by fusing the ferrocyanides alone or with alkali metal or alkali carbonate :

$$K_4Fe(CN)_6 = 4KCN + Fe + 2C + N_2$$
$$Na_4Fe(CN)_6 + 2Na = 6NaCN + Fe$$
$$K_4Fe(CN)_6 + K_2CO_3 = 5KCN + KCNO + CO_2 + Fe.$$

Sodium cyanide is manufactured by the **Castner process.** Ammonia gas is passed over fused sodium heated at 300°–400° in an iron retort :

$$2Na + 2NH_3 = 2NaNH_2 + H_2.$$

The fused sodamide is poured over red-hot charcoal, when it reacts to form sodium cyanamide $Na_2{:}N{\cdot}CN$ and then cyanide :

$$2NaNH_2 + C = Na_2{:}N{\cdot}CN + 2H_2$$
$$Na_2{:}N{\cdot}CN + C = 2NaCN.$$

The pure cyanide, m.p. 563·7°, is precipitated by hydrogen cyanide gas from alcoholic sodium hydroxide.

Potassium cyanide is made by the **Beilby process.** Ammonia gas is passed over a mixture of fused potassium carbonate and carbon :

$$K_2CO_3 + C + 2NH_3 = 2KCN + 3H_2O.$$

The pure fused cyanide is decanted and cast in moulds.

Very pure potassium cyanide, m.p. 634·5°, is formed in cubes by recrystallising from liquid ammonia (Hackspill and Grandadam, 1926).

Cyanates.—Fused potassium and sodium cyanides are powerful *reducing agents* : many metallic oxides are converted into metals and a cyanate is formed : $KCN + PbO = KCNO + Pb$, which may be extracted with water. When the solution is acidified, **cyanic acid** HCNO is formed, but is almost completely hydrolysed to ammonia and carbon dioxide :

$$HCNO + H_2O = NH_3 + CO_2.$$

Potassium cyanate is prepared by throwing a powdered mixture of anhydrous potassium ferrocyanide and potassium dichromate in small portions into a heated iron dish, extracting the product with hot methylated spirit, and crystallising by cooling (Bell, 1875 ; Erdmann, *Ber.*, 1893, **26**, 2438).

Pure cyanic acid is a colourless liquid obtained by heating crystalline **cyanuric acid** $(CNOH)_3$, obtained by distilling urea : $3CO(NH_2)_2 = (CNOH)_3 + 3NH_3$.

Ammonium cyanate NH_4CNO is obtained in solution by mixing concentrated solutions of potassium cyanate and ammonium chloride and is readily converted on heating into the isomeric urea : $NH_4{\cdot}CNO = CO(NH_2)_2$ (Wöhler, 1828).

The cyanates probably contain the *iso*cyanate radical [O=C=N]′ (see p. 560).

A cyanate (or thiocyanate) with cobalt chloride and acetic acid gives a bright blue colour due to the formation of the ion $Co(CNO)_4''$ (or $Co(CNS)_4''$).

Thiocyanates (probably *iso*thiocyanates) are formed when alkali cyanides are fused with sulphur: $KCN + S = KNCS$, or ammonium cyanide reacts with yellow ammonium sulphide: $NH_4CN + (NH_4)_2S_2 = NH_4NCS + (NH_4)_2S$. The free acid is known.

Oxycyanogen $(NCO)_2$ is formed by the reaction $2AgNCO + I_2 = 2AgI + (NCO)_2$ (Hunt, *J.A.C.S.*, 1932, **54**, 907), and **thiocyanogen** $(NCS)_2$ by the reaction $Pb(NCS)_2 + Br_2 = PbBr_2 + (NCS)_2$ (Söderbäck, 1919). They are solids called **pseudo-halogens**. They liberate iodine from iodides, combine with metals by addition, and can be titrated with thiosulphate like iodine: $(NCS)_2 + 2S_2O_3'' = S_4O_6'' + 2NCS'$ (Kaufmann, etc., 1924–26; Birkenbach, etc., 1925–31).

CHAPTER XVIII

SILICON AND FOURTH GROUP METALS

Silicon

NEXT to oxygen (50 p.c.) silicon (26 p.c.) is the most abundant element in the earth's crust. It occurs as *silica* SiO_2 (quartz, and less pure as flint, sand, etc.) and *silicates*; granite and similar primitive rocks contain 20–30 p.c. of silicon.

Silica was at first classed as an "earth," although Otto Tachenius in 1666 pointed out that it has acidic properties, dissolving in alkali to form a solution from which it is precipitated by a stronger acid. In 1809 Gay-Lussac and Thenard obtained silicon as a brown powder by heating potassium in silicon fluoride gas: $SiF_4 + 4K = Si + 4KF$, but did not examine it. Berzelius in 1823 prepared it by heating potassium fluosilicate with potassium: $K_2SiF_6 + 4K = Si + 6KF$, and determined its chief properties.

Silicon forms alloys with metals, but in most of its properties it is a non-metallic element resembling carbon, and also shows many resemblances to boron. It has a great affinity for oxygen: $[Si] + (O_2) = [SiO_2] + 191$ k. cal., so that silica is reduced only at high temperatures by carbon, or otherwise by powerful reducing agents such as magnesium. The halogen compounds (*e.g.* SiF_4 and K_2SiF_6, see above) are reduced by heating with alkali metals.

In the laboratory silicon is most conveniently prepared by heating silica with magnesium powder (Gattermann, *Ber.*, 1889, **22**, 186; Vigouroux, *Ann. Chim.*, 1897, **12**, 5): $SiO_2 + 2Mg = 2MgO + Si$.

EXPT. 1.—Two g. of a mixture of 5 parts of powdered quartz or *thoroughly dried* amorphous silica, 3 parts of magnesium powder and 2 parts of calcined magnesia to moderate the reaction, are heated in a covered silica crucible. The mass glows when vigorous reaction occurs. After cooling the magnesia is dissolved out by hydrochloric acid, and the silicon washed in a platinum dish with hydrofluoric and sulphuric acids to remove silica; it is dried by heating in hydrogen and the purity can reach 96–97 p.c.

The so-called *amorphous silicon* so prepared is a light chestnut-brown hygroscopic powder, s. g. 2·35, which is shown by the X-ray spectrum to consist of minute octahedral crystals, the only crystalline form of silicon known. It burns only superficially when heated in air but brilliantly in oxygen at 400°, ignites spontaneously in fluorine and burns in chlorine at 450° and in bromine vapour at 500°; it reacts without incandescence with iodine vapour at a red heat, with sulphur vapour at 600°, nitrogen at 1000°, and carbon and boron (forming SiC and SiB_3) at 2000°. It is insoluble in acids except a mixture of nitric and hydrofluoric acids, but dissolves readily in concentrated alkalis evolving hydrogen (p. 284), and in fused sodium carbonate: $Si + 2Na_2CO_3 = Na_4SiO_4 + 2CO$, and potassium nitrate. It slowly decomposes steam at a red heat:

$Si + 2H_2O = SiO_2 + 2H_2$. When strongly heated in a closed crucible it fuses (m.p. 1420°) and solidifies on cooling to a crystalline mass.

Octahedral crystals of silicon, which may be orange-coloured and transparent, or black and opaque, are formed by strongly heating potassium fluosilicate with sodium and zinc, or with aluminium : $3K_2SiF_6 + 4Al = 4AlF_3 + 6KF + 3Si$, and dissolving the excess of metal from the alloy with hydrochloric acid (Deville, 1854 ; Wöhler, 1856). Zinc gives needle-shaped crystals, aluminium six-sided plates, but both are made up of regular octahedra. The crystals, s. g. 2·49, scratch glass. Another variety, s. g. 2·42, is formed by crystallising from molten copper or silver. Crystalline silicon does not burn in oxygen even when strongly heated, but ignites spontaneously in fluorine and burns when heated in chlorine. It is attacked by a mixture of nitric and hydrofluoric acids and by fused sodium carbonate.

Silicon is made technically, *e.g.* at Niagara, by heating silica and carbon in the electric furnace (Moissan, 1895) : $SiO_2 + 2C = Si + 2CO$, or by heating silica and calcium carbide : $SiO_2 + CaC_2 = Si + Ca + 2CO$. It is a hard grey crystalline mass, with the appearance and electric conductivity of graphite, m.p. 1420°, b.p. 2600°, and is used in making alloys (silicon-bronze, manganese-silicon-bronze), on which it confers hardness and tensile strength. Silica is also reduced when heated with carbon and iron in the blast furnace and cast iron always contains silicon. Iron containing carbon and more than 15 p.c. of silicon (*ironac*, *tantiron*, *duriron*, *narki*, etc.) is resistant to acids except hydrochloric, which requires an alloy with 50 p.c. of silicon.

A mixture of silica, aluminium powder and sulphur ignites and burns violently in a thermit reaction (p. 738), and when the regulus is treated with water and boiling dilute hydrochloric acid crystalline silicon remains (Kühne, 1902 ; Fowles, *Lecture Experiments in Chemistry*, 1937, 286).

Silicon Hydrides

Silicon forms the following hydrides, which are analogous to hydrocarbons ; the stability decreases from SiH_4 to Si_4H_{10} :

SiH_4	Si_2H_6	Si_3H_8	Si_4H_{10}
gas	gas	liquid	liquid
m.p. −185°, b.p. −112°	m.p. −132·5°, b.p. −14·5	m.p. −117°, b.p. 53°	m.p. −90°, b.p. 109°

Some solid hydrides are also described. No unsaturated hydrides (analogous to ethylene) are known, and only one form of Si_4H_{10} (corresponding with normal butane) has been prepared.

Silicon and hydrogen may combine slightly at the temperature of the electric arc : $Si + 2H_2 \rightleftharpoons SiH_4$, but silicon hydride is usually prepared by the action of hydrochloric acid on magnesium silicide : $Mg_2Si + 4HCl = 2MgCl_2 + SiH_4$.

When a mixture of 2 pt. of magnesium powder and 1 pt. of *dry* amorphous silica is heated in a silica crucible a violent reaction occurs and **magnesium silicide**, which consists mainly of Mg_2Si, is formed as a bluish crystalline mass. This when treated with dilute hydrochloric acid in a flask from which air has been displaced by hydrogen, evolves a spontaneously inflammable mixture of silicon

hydrides and hydrogen (Wöhler, 1858). If the gas is bubbled through water, each bubble ignites in contact with the air and burns with a luminous flame, producing a vortex ring of finely divided silica: $SiH_4 + 2O_2 = SiO_2 + 2H_2O$. A better yield is obtained by dropping magnesium silicide into a solution of ammonium bromide in liquid ammonia in a slow stream of hydrogen (Johnson and Hogness, 1934): $Mg_2Si + 4NH_4Br = 2MgBr_2 + SiH_4 + 4NH_3$.

The gas, after washing with water and drying with calcium chloride and phosphorus pentoxide, is passed through a tube cooled in liquid air and a liquid mixture of silicon hydrides condenses, from which by fractionation the following compounds may be isolated (Stock, etc., 1916 f.; *The Hydrides of Boron and Silicon*, 1933).

1. **Monosilane** SiH_4, a colourless gas, stable at ordinary temperature, spontaneously inflammable if mixed with the other hydrides and sometimes if pure; relative density 16·02 (H = 1); decomposed when passed through a red-hot tube to twice its volume of hydrogen: $SiH_4 = Si + 2H_2$, and by caustic alkalis: $SiH_4 + 2KOH + H_2O = K_2SiO_3 + 4H_2$, giving four times the volume of hydrogen. The gas precipitates copper silicide Cu_2Si from copper salts, and silver from silver salts: $4AgNO_3 + SiH_4 = Si + 4Ag + 4HNO_3$.

Pure monosilane is obtained (Friedel and Ladenburg, 1871) by heating **triethyl silicoformate** with sodium: $4SiH(OC_2H_5)_3 = SiH_4 + 3Si(OC_2H_5)_4$ (**ethyl orthosilicate**). Triethyl silicoformate, the silicon analogue of orthoformic ester $CH(OC_2H_5)_3$, is obtained by the action of silicon chloroform on absolute alcohol or sodium ethoxide: $SiHCl_3 + 3C_2H_5ONa = SiH(OC_2H_5)_3 + 3NaCl$.

2. **Disilane** Si_2H_6, a colourless gas, stable at ordinary temperature but rapidly decomposed at 300°; relative density 31·7; inflames in air; soluble in benzene and carbon disulphide; decomposed by alkalis: $Si_2H_6 + 2H_2O + 4KOH = 2K_2SiO_3 + 7H_2$.

3. **Trisilane** Si_3H_8, a colourless liquid, decomposing spontaneously at ordinary temperature. Si_2H_6 and Si_3H_8 react vigorously with carbon tetrachloride and chloroform: $2CCl_4 + Si_2H_6 = 2SiCl_4 + 2C + 3H_2$.

4. **Tetrasilane**, Si_4H_{10}, a colourless liquid, less stable than Si_3H_8.

5. **Solid hydrides** probably Si_5H_{12} and Si_6H_{14}, remain after fractionation. Brown solid **silicon dihydride** $(SiH_2)_x$ is obtained by the action of glacial acetic acid or a solution of HCl in alcohol on CaSi (prepared by heating Ca and Si at 1050°) (Schwarz and Heinrich, 1935).

Dry hydrogen chloride in presence of aluminium chloride reacts with SiH_4 to form SiH_3Cl (m.p. −118°, b.p. −30·5°) and SiH_2Cl_2 (m.p. −122°, b.p. 8·5°): $SiH_4 + HCl = SiH_3Cl + H_2$. Solid bromine at −80° forms SiH_3Br (m.p. −94°, b.p. 1·9°) and SiH_2Br_2 (m.p. −70·1°, b.p. 66°). Water and SiH_3Br form a colourless inflammable gas **disiloxane** $(SiH_3)_2O$, m.p. −144°, b.p. −15·2°: $2SiH_3Br + H_2O = (SiH_3)_2O + 2HBr$. SiH_2Br_2 gives **protosiloxane**, which rapidly polymerises, $(SiH_2O)_x$: $SiH_2Br_2 + H_2O = SiH_2O + 2HBr$.

Silicides

Several compounds of silicon with metals are known. **Lithium silicide** Li_6Si_2 is formed in deep blue crystals by heating lithium and silicon to redness and removing the excess of lithium by liquid ammonia. It reacts violently with water, evolving Si_2H_6. Silicides of **magnesium** Mg_2Si (blue octahedra), **calcium**

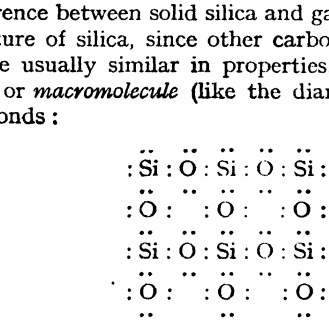
$CaSi_2$, **strontium** $SrSi_2$ and **barium** $BaSi_2$ are formed by strongly heating the metals with silicon (and dissolving excess of magnesium with ethyl iodide and ether) : they are decomposed by acids, evolving silicon hydrides. Other silicides described, mostly formed in the electric furnace, are :

CeSi, $CeSi_2$.
$TiSi_2$, $ZrSi_2$, $ThSi_2$.
VSi_2, $TaSi_2$.
Cr_2Si, $CrSi_2$, Mo_2Si, $MoSi_2$, W_2Si_3, WSi_2, USi_2.
Mn_2Si, MnSi.
FeSi, Co_2Si, CoSi, $CoSi_2$, $CoSi_3$, Ni_2Si, NiSi, Pt_2Si, PtSi, RuSi, PdSi.

They mostly form hard crystals with metallic lustre and high m.ps. and are refractory.

Silica and Silicic Acids

The great difference between solid silica and gaseous carbon dioxide is due to the peculiar structure of silica, since other carbon and silicon compounds (*e.g.* CCl_4 and $SiCl_4$) are usually similar in properties. The structure of silica is a " giant molecule " or *macromolecule* (like the diamond), and all the atoms are linked by strong bonds :



Silica occurs both *crystalline* and *amorphous*. The three main crystalline forms are *quartz*, *tridymite* and *cristobalite*, but there are different modifications of each, with definite transition points (Fenner, 1912–14).

(1) **α-quartz** (tetartohedral hexagonal) $\overset{573°}{\rightleftharpoons}$ **β-quartz** (hemihedral hexagonal)

(2) **β-quartz** $\overset{870°\pm10°}{\rightleftharpoons}$ **β-tridymite** (holohedral hexagonal)

(3) **β-tridymite** $\overset{1470°\pm10°}{\rightleftharpoons}$ **β-cristobalite** (cubic).

β-tridymite and β-cristobalite have the following transition temperatures with metastable modifications having lower optical symmetry :

(4) **β-tridymite** $\overset{163°}{\rightleftharpoons}$ **β_1-tridymite** $\overset{117°}{\rightleftharpoons}$ **α-tridymite** (biaxial, perhaps rhombic).

(5) **β-cristobalite** $\overset{198°-275°}{\rightleftharpoons}$ **α-cristobalite** (biaxial).

There may be a fourth form of tridymite with a transition point at 440°. The relations among the forms is shown *diagrammatically* in Fig. 229. Quartz is the only *stable* form below 870° ; the three tridymites and α-cristobalite below 870° are metastable. The transitions (1), (4) and (5) above occur rapidly, but (2) and (3), as well as the transition β-cristobalite ⇌ liquid at the m.p. 1710°, are sluggish. Between 870° and 1470° β-tridymite is the stable form ; from 1470° to 1710° β-cristobalite.

Silica glass, formed by rapid cooling of the liquid, exists from ordinary temperature to 1000° or above, when it begins to crystallise, at an appreciable rate above 1250°. In devitrifying it always forms cristobalite, unless a flux is present. Cristobalite tends to change into tridymite rather than quartz; the direct transformation of quartz into tridymite without a flux is doubtful.

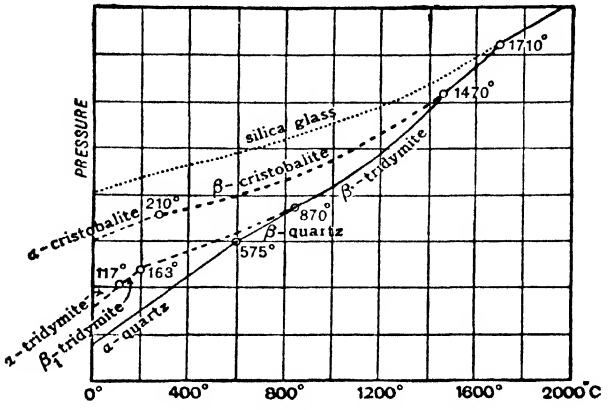


FIG. 229.—Phase diagram of silica.

Since quartz changes to cristobalite (or tridymite) with expansion, silica bricks shatter when quickly heated below about 500° unless a large proportion of the quartz has been converted into the form stable at high temperatures by previous heat treatment: this form remains metastable on cooling.

Quartz (s. g. 2·648) or *rock-crystal* occurs sometimes in clear colourless crystals, but more often in opaque ("milky") or coloured masses ("smoky-quartz," "cairngorm.") Coloured varieties (*e.g.* purple *amethysts*) are gems. *Sand* consists mainly of grains of quartz which remain after the disintegration or "weathering" of rocks.

The crystalline form of quartz, apparently hexagonal, is really a tetartohedral trigonal trapezohedron with lower symmetry. Some crystals have hemihedral facets (*s*, *x*, Fig. 124) and are optically active. The atomic structures of crystalline silica have been investigated by X-ray analysis. In all of them each silicon is surrounded by four oxygens and each oxygen by two silicons, and all the valencies are used up. The simplest structure is cristobalite: if the diamond lattice (Fig. 196) is taken, and a silicon atom placed in the position of each carbon atom and an oxygen atom at the middle point of each bond (Fig. 230) the cristobalite structure results. This involves a distortion of the valency bond angle of oxygen from the normal value of about 100° (p. 268) to 180°, and in the other forms of silica the 100° angle is more nearly approached. In quartz the atoms are arranged with a screw-like symmetry, corresponding with its optical activity, and the oxygen valency angle is about 145°.

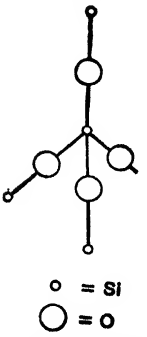


FIG. 230.—Structure of cristobalite.

Tridymite (s. g. 2·26) occurs more rarely than quartz, in minute hexagonal crystals usually in the form of six-sided plates (Fig. 231), *e.g.* in cavities of the trachytic rocks of Mexico and Stenzelberg, and in solidified magmas and lavas.

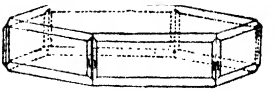


FIG. 231.—Crystal of tridymite.

Cristobalite (s. g. 2·32) is a cubic crystalline variety obtained by heating powdered amorphous (fused) silica at 1500°. It is stable at high temperatures and is found in some volcanic rocks and in meteorites.

Amorphous silica.—All varieties of silica soften below 1600°, fuse in the oxyhydrogen blowpipe at 1710°, and boil in the electric furnace at 2220° (Ruff and Schmidt, 1921). They become plastic before fusion and may be worked and blown like glass, or drawn into thread. The amorphous vitreous product, s. g. 2·2, called *silica glass*, first made by Gaudin in 1839 (Bottomley, *J.S.C.I.*, 1917, **36**, 577) has a very small coefficient of expansion (cubical coefficient = 5×10^{-7}) and may be heated to redness and quenched in cold water without fracture (quartz crystals easily crack when heated). It is transparent to the ultra-violet whilst ordinary glass is opaque. Hydrogen diffuses easily through heated silica glass, helium even at room temperature and very rapidly at 510°, and oxygen appreciably at 600° (Williams and Ferguson, *J.A.C.S.*, 1922, **44**, 2160).

Besides transparent fused silica a translucent variety (*vitreosil*) is manufactured by fritting sand with an electrically-heated carbon rod or plate, evolution of gas from which prevents the fused silica from sticking to the carbon heater.

Pure amorphous silica is obtained as a fine white powder by decomposing pure silicon tetrachloride with water and heating the resulting gel. Amorphous silica is usually prepared by adding hydrochloric acid to sodium silicate solution (*water glass*), evaporating on a water bath, when the silica gel becomes granular and insoluble, washing with hot distilled water, drying and heating to redness.

Amorphous silica which has been heated is insoluble in cold water and acids except phosphoric and hydrofluoric, but dissolves in hot concentrated alkalis. At high temperatures silica, being non-volatile, displaces volatile acid anhydrides from salts: $SiO_2 + Na_2SO_4 = Na_2SiO_3 + SO_3$.

Silica is appreciably soluble in superheated water (0·1 p.c. at 300°) and in hot slightly alkaline water, so that it occurs in hot springs and geysers (Black, 1794), which deposit silica at the mouths. Dissolved silica passing into wood, etc., produces *petrifaction*. Silica is found in the straw of cereals, bamboo cane, the weed horse-tail, the feathers of some birds, and sponges. *Kieselguhr* and *tripoli* consist of the siliceous skeletons of extinct diatoms. If hydrated silica is heated with a solution of sodium silicate in a sealed glass tube, small crystals of quartz are formed. Larger crystals are produced by the prolonged heating at 250° in a sealed tube of a 10 p.c. solution of colloidal silica. Spezia (1905–9) obtained quartz crystals more than 1 cm. long from solutions of quartz in sodium silicate solution kept for some months at 330°.

By adding acid to a concentrated solution of sodium silicate a jelly of colloidal hydrated silica is formed, called *silica gel*. This may be broken up, washed and dried, when it forms a glassy amorphous solid used as an adsorbent. *Opal* is a natural form of amorphous hydrated silica.

Silica gel dried in the air retains about 16 p.c. of water. At 100°, 13 p.c. of water remains and the silica is then insoluble. On further heating water is gradually lost; according to van Bemmelen (1897) the vapour-pressure curve shows no breaks indicative of hydrates but Tammann (quoted by Zsigmondy, 1911) found breaks corresponding with **orthosilicic acid** H_4SiO_4 and **metasilicic acid** H_2SiO_3. Maschke (1872) noticed that the clear gel becomes white and opaque when some water is removed but clears again on further drying. Water-vapour readmitted to the partly dehydrated mass is reabsorbed, but the pressure is higher than in the corresponding part of the dehydration curve. After heating at 300° the gel contains about 4 p.c. of water and only after prolonged heating at 900°–1000° is all the water lost (Holmes and Anderson, *Ind. Eng. Chem.*, 1925, **17**, 280). No one now regards this amorphous gel as a definite hydrate or a silicic acid.

When a dilute solution of sodium silicate is poured into excess of dilute hydrochloric acid the silica is not precipitated but forms a clear colloidal solution or *silica sol* which may be dialysed (Graham, 1861). The solution may be concentrated by boiling and by further evaporation over sulphuric acid until it contains 14 p.c. of SiO_2; it is then a clear tasteless liquid with a feebly acid reaction, readily coagulated to a bluish-white nearly transparent gel. The sol is more stable in presence of small amounts of hydrochloric acid or sodium hydroxide, but is coagulated by sodium carbonate or phosphate.

Quite different from the amorphous gel are the granular powders of hydrated silica usually called **silicic acids.**

By heating at 1150° quartz powder and sodium carbonate in the proportions to form Na_2SiO_3, $Na_2Si_2O_5$ and $Na_4Si_3O_8$, treating with 80 p.c. sulphuric acid at 10°, and washing the granular white powders with alcohol and ether to remove 5 p.c. excess of water, Tschermak (1909) obtained what he regarded as *metasilicic* (H_2SiO_3), *disilicic* ($H_2Si_2O_5$) and *trisilicic* ($H_4Si_3O_8$) *acids*. The existence of H_2SiO_3 and $H_2Si_2O_5$ but not $H_4Si_3O_8$ was confirmed by Schwarz and co-workers (1924 f.) from the vapour pressure dehydration curves, and in this way Simon and Rath (1931) claim to have detected five silicic acids, with $\frac{1}{2}$, $\frac{2}{3}$, 1, 2 and 4 H_2O per molecule of SiO_2.

Silicic acid *esters* are known. *Ethyl orthosilicate* $(C_2H_5)_4SiO_4$ (b.p. 60°–62°/12 mm.) and *methyl orthosilicate* $(CH_3)_4SiO_4$ (b.p. 25°/12 mm.) are formed by the action of $SiCl_4$ on the anhydrous alcohols; in presence of a little water *ethyl metasilicate* $(C_2H_5)_2SiO_3$, b.p. 104°–6°, is obtained. By the slow hydrolysis of ethyl orthosilicate, orthosilicic acid is formed (Thiesen and Körner, 1930): $(C_2H_5)_4SiO_4 + 4H_2O = H_4SiO_4 + 4C_2H_5OH$.

Sodium silicate (*soluble glass*) is made by melting sodium carbonate with powdered quartz or pure sand in a reverberatory furnace at a high temperature. Probably various silicates are formed, *e.g.*: $Na_2CO_3 + SiO_2 = Na_2SiO_3 + CO_2$. A mixture of sodium sulphate (*saltcake*) and powdered charcoal may be used:

$$Na_2SO_4 + 2C = Na_2S + 2CO_2$$
$$Na_2S + 3Na_2SO_4 + 4SiO_2 = 4Na_2SiO_3 + 4SO_2.$$

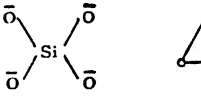
The greenish-blue glass (brown if sodium sulphide is present), when broken up and heated with water under pressure in autoclaves, slowly dissolves to a

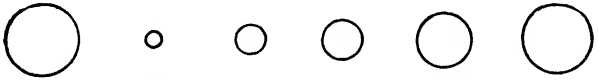
thick solution known as *water glass*, which may contain 2 to 4 molecules of SiO_2 to 1 molecule of Na_2O. It is strongly alkaline owing to hydrolysis and is sometimes added to soap. Water glass is used in treating cement floors to reduce dust and abrasion, for preserving eggs, and other purposes. Crystalline **sodium metasilicate** $Na_2SiO_3,5H_2O$ is readily soluble in cold water and is used in laundries.

By grinding the ordinary sodium silicate glass finely and heating with a little water a clear glass is formed which is soluble in cold water (Caven, *J.S.C.I.*, 1918, **37**, 63).

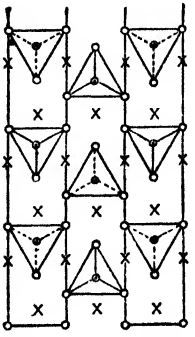
Structure of Silicates

In the silicates the fundamental unit is the **orthosilicate ion** SiO_4^{4-}, in which the silicon is tetrahedrally surrounded by four oxygens. The distance Si to O is 1·62 A. and the distance O to O is 2·7 A., as determined by X-ray methods (W. L. Bragg, *The Atomic Structure of Minerals*, Oxford, 1937; Pauling, *J.A.C.S.*, 1929, **51**, 1010; *The Nature of the Chemical Bond*, 1940, 385). Four electrons are drawn from the oxygens O^{2-} to the silicon Si^{4+}, and the ion has the negative charge uniformly distributed over the four oxygens, the central silicon being neutral and each oxygen having unit negative charge. The tetrahedral structure of the ion is represented in projection as shown, oxygen being shown as ○, and the silicon as •, the silicon being shown inside the oxygen at the apex. Each oxygen is joined to silicon by only one link and is not joined to other oxygens, the sides of the tetrahedron merely indicating the arrangement in space.





1. In the **orthosilicates** the SiO_4^{4-} ions are independent and the charges are balanced by positive charges of cations packed in the lattice in the interstices of the silicate ions. The radii of the metal (and silicon) ions are, except in the case of calcium and alkali metals, small compared with the radius of the oxygen ion, so that the structure is practically determined by the packing of the oxygens.



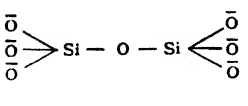
In orthosilicates the positive ions are usually bivalent, *e.g.* in olivine Mg_2SiO_4 the SiO_4^{4-} tetrahedra are arranged alternately orientated in parallel rows with Mg^{2+} ions interposed, as shown. Each Mg^{2+} (shown as ×) is surrounded by 6 oxygens slightly distorted from the ideal octahedral arrangement.

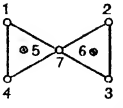
2. In silicates other than orthosilicates we distinguish **two types of oxygen linkage**:

(*a*) The oxygen atom belongs to two silicon atoms, *i.e.* is *linked on both sides to silicon*, when its valencies are saturated and the linkage is covalent.

(*b*) The oxygen atom is *linked on one side only to silicon*, when it has one negative charge which can be neutralised by a positive cation :

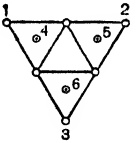
For example, the ion $Si_2O_7^{6-}$ may be represented as two tetrahedra meeting in a corner sharing an oxygen. The oxygens 1 to 6 (type *b*) each contribute -1 to the valency, but oxygen 7 (type *a*) is linked on both sides and is neutral.



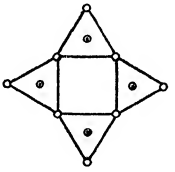


3. The various more complicated **silicate ions** may be built up from the fundamental SiO_4^{4-} group in the manner shown below. Each arrangement, which contains linkages of types *a* and *b*, forms a self-contained anion, neutralised in the silicates by positive cations suitably arranged in the lattice. The anions may consist of :

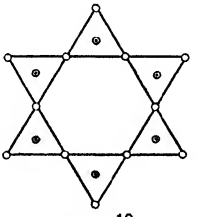
(*A*) **Rings** of 3, 4 or 6 silicon atoms with an equal number of oxygen atoms linked on both sides between them. The valency of each group is given by the number of oxygen atoms linked on *one side* only to silicon (case *b*), *e.g.* numbers 1 to 6 in the first figure :



$Si_3O_9^{6-}$



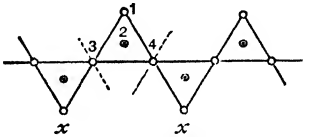
$Si_4O_{12}^{8-}$



$Si_6O_{18}^{12-}$

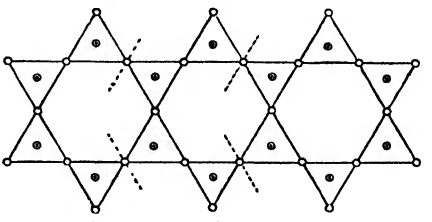
(*B*) **Chains, fibres** or **bands,** formed by linking pairs of silicon atoms through oxygen and capable of extending indefinitely in length. The valency is again -1 for each oxygen singly linked to silicon (type *b*). Two arrangements may be distinguished.

(*α*)



Metasilicate $[SiO_3^{2-}]_n$, *e.g.* $Ca^{2+}Mg^{2+}(SiO_3^{2-})_2$.

(*β*)



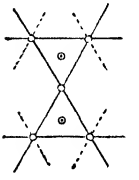
Metatetrasilicate $[Si_4O_{11}^{6-}]_n$, *e.g.* $Ca_2Mg_4(Si_4O_{11})_2.Mg(OH)_2$.

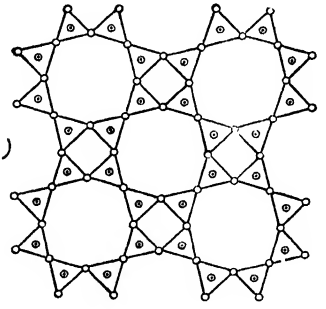
In the first (*α*) each unit as shown between dotted lines contains one Si singly linked to two oxygens, 1 and 2, of type *b*, giving the valency -2, and sharing two half-oxygens, 3 and 4, of type *a* (valency zero) with two other silicons ; *i.e.* each silicon is associated with $2 + 2 \times \frac{1}{2} = 3$ atoms of oxygen in all,

making up the metasilicate ion, SiO_3^{2-}. The end units, making up only a small fraction of the lattice, are disregarded.

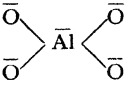
The second arrangement (β) is formed by joining two (α) arrangements by sharing the oxygens marked *x*, thus forming a band from a chain. The unit shown between dotted lines contains 4 silicons associated with $9 + 4 \times \frac{1}{2} = 11$ oxygens in all, and of these 6 are singly linked to silicon (type *b*), giving the valency -6 to the unit.

(*C*) **Sheets** extending indefinitely in area, formed by linking bands of type $B\beta$ by sharing oxygens marked *x*. Three oxygens of each tetrahedron are now linked on both sides and have zero valency, whilst one oxygen is only singly linked and has the valency -1. The unit of such an arrangement is shown between dotted lines, and is seen to be $Si_2O_5^{2-}$; two silicon atoms are linked with $3 + 4 \times \frac{1}{2} = 5$ oxygens, and there are 2 singly linked oxygens (type *b*) giving the valency -2. It is unnecessary to draw the arrangement $[Si_2O_5^{2-}]_n$ in full, as it is easily visualised as formed of two $B\beta$ strips. This is the ion of the disilicates, *e.g.* talc, $Mg_2(Si_2O_5)_2$, $Mg(OH)_2$. In mica, one in four of the tetrahedral groups of oxygens surrounds aluminium instead of silicon (see below). The arrangement (γ) is also a disilicate, the unit being again $Si_2O_5^{2-}$. Any arrangement of SiO_4 tetrahedra linked through oxygens in sheets gives the same unit ion.





(*D*) If we imagine every corner of the SiO_4^{4-} tetrahedron linked through oxygen we obtain a **three-dimensional lattice**. Every oxygen is now shared and there are no free valencies. The resulting structure contains two oxygens to every silicon atom and is electrically neutral. The result is silica, the structure of which has been represented in this way on p. 499. If, however, a silicon is replaced by an aluminium ion, of charge $+3$ instead of $+4$, tetrahedrally surrounded by four oxygens, the central Al now has a charge -1, since it is unable to neutralise the 4 negative oxygen charges drawn to the centre. This extra charge may be balanced in the lattice by additional cations. The arrangement is present in the **aluminosilicates**: *e.g.* $(NaAl)Si_3O_8$ forms $CaAl_2Si_2O_8$ by replacing $^{+}_{Na}Si$ by $^{++-}_{Ca}Al$.



By replacing some silicon in silica by aluminium we obtain a large negatively charged lattice, like a vast extended acid radical, which can absorb cations to assume electrical neutrality. Examples of such arrangements are the zeolites, the sponge-like lattice of which remains unaltered when metal ions are exchanged, *e.g.* Ca^{2+} for $2Na^{+}$. This explains the ready exchange of such ions in water softeners (p. 676).

The structure of aluminosilicates and clay minerals (Pauling *Proc. Nat. Acad. Sci.*, 1930, **16**, 123, 578; Marshall, *Science Progress*, 1936, **30**, 422) is regarded

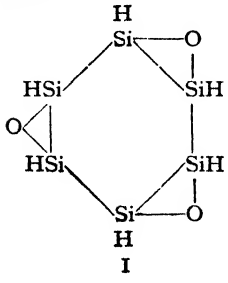
as made up of sheets of $Si_2O_5^{2-}$ anions, of brucite $Mg(OH)_2$, and of gibbsite $Al(OH)_3$, the last two having layer lattices. These sheets are formed by insertion of Si^{4+}, Al^{3+} and Mg^{2+} ions into the interstices of a double layer of closely-packed O^{2-} or OH^- ions; Al may replace some Si or $2Al^{3+}$ may be replaced by $3Mg^{2+}$. The composite sheets are then formed by sharing oxygen atoms.

When the sheets are electrically neutral, as in talc, the minerals are soft and easily cleaved; when they are charged and bound electrostatically by univalent K^+ ions, as in mica, the mineral is harder and less easily cleaved, and when they are bound by bivalent Ca^{2+} ions of higher charge the material is hard and brittle. In chlorite, mica-like anion sheets interleave with brucite-like cation sheets.

Of the clay minerals (p. 425), *allophane* is amorphous. *Montmorillonite* shows the same X-ray pattern as *pyrophillite*, which occurs crystalline in slates; the pyrophillite-like layers in montmorillonite recede and approach as the substance swells or shrinks by taking up or losing water, and each layer is formulated as Al_2O_3, $4SiO_2$, $H_2O + nH_2O$. *Beidellite*, a colloidal soil mineral, has the same formula. In *halloysite* there are alternating layers of hydrated silica $Si_2O_3(OH)_2$ and gibbsite $Al(OH)_3$, so that the ideal formula is $Al_2O_3,2SiO_2,4H_2O$, and *kaolinite* $Al_2O_3,2SiO_2,2H_2O$ is derivable from it by loss of water between the layers.

Since the Al^{3+} ion is of medium size it can replace silicon in a tetrahedral arrangement of oxygens in SiO_4 (p. 503), forming aluminates and alumino-silicates, and can also replace Mg, Fe^{II} and Fe^{III} in an octahedral arrangement of oxygens, as in micas. In potash felspar, where Al^{3+} replaces Si^{4+} in $4SiO_2$, the group has a valency -1 and is associated with a K^+ ion: $[(SiO_2)_3AlO_2]K$.

Siloxene.—By the action of *concentrated* hydrochloric acid on calcium silicide Wöhler (1863) obtained a yellow solid which he called *silicone* and formulated $Si_4H_4O_3$. Hönigschmid (1909) formulated it $(SiH)_3O_3$. It is very stable but when exposed to light under water it evolves hydrogen and forms a white substance which Wöhler called *leucone* and formulated $Si_4H_4O_5$ or $Si_4H_3O_5$, and Hönigschmid $Si_3H_3O_4$. Wöhler found that calcium silicide with *dilute* hydrochloric acid gives "colourless transparent leaves like mother of pearl," which when dried inflame on exposure to air. Kautsky (1921) at first formulated this as $Si_4H{\cdot}OH$, obtaining it from dilute alcoholic hydrogen chloride and calcium silicide, but later (1924) he formulated it as a ring compound (I) and called it **siloxene**:



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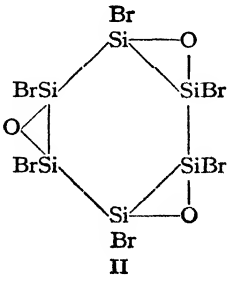
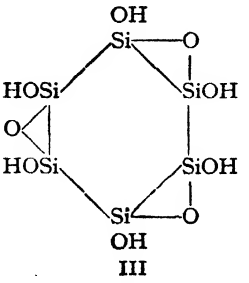


II



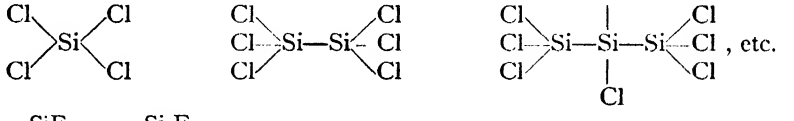
III

Siloxene is luminiscent, inflames spontaneously in air, and is decomposed by light and by water. It appears to be a layer compound like graphitic oxide (p. 443), crystallising in thin sheets. It absorbs dyes, which apparently penetrate

between the sheets. By the action of bromine under carbon disulphide, or of hydrobromic acid, hydrogen is replaced and yellow **silical bromide** (II) is formed, but excess of bromine breaks the ring and forms $Br_3Si{\cdot}O{\cdot}SiBr_3$. By the action of water on silical bromide the bromine is replaced in steps by hydroxyl, forming compounds containing from 1 (yellow) to 6 (black) OH groups, the last (**silical hydroxide,** III) being a weak base. Similar compounds containing NH_2 are formed by the action of ammonia, and are weak bases. Wöhler's silicone is probably a mixture of I and III.

Halogen Compounds of Silicon

The following halogen compounds of silicon have been described. Those containing more than one atom of silicon no doubt contain chains of quadrivalent silicon atoms :



	SiF_4	Si_2F_6
	gas	gas
b.p.	−65°/941 mm.	−19·1°
m.p.	−77°/2 atm.	−18·7°/780 mm.

	$SiCl_4$	Si_2Cl_6	Si_3Cl_8	Si_4Cl_{10}	Si_5Cl_{12}	Si_6Cl_{14}	$Si_{10}Cl_{22}$
	liquid	liquid	liquid	liquid	liquid	solid	viscous liquid
b.p.	56·8°	145°	210°–215°	150°/15 mm.	190°/15 mm.	200° in vac.	215° (20° in
m.p.	−70°	−1°	−67°	—	—	170°	vacuum.)

	$SiBr_4$	Si_2Br_6	Si_3Br_8	Si_4Br_{10}
	liquid	solid	solid	solid
b.p.	153°	240°	265°	decomp. at 185°
m.p.	5°	95°	95°	—

	SiI_4	Si_2I_6
	solid (cubic)	solid (hexagonal)
b.p.	290°	—
m.p.	120·5°	250°

All these compounds are colourless. A number of mixed halogen compounds : $SiBr_3Cl$, $SiBr_2Cl_2$, $SiBrCl_3$, $SiBr_3I$, $SiBr_2I_2$, $SiBrI_3$, also orange-coloured Si_2I_4 and amorphous $(SiCl)_x$, are described.

Analogous to chloroform are the compounds :

$SiHF_3$	$SiHCl_3$	$SiHBr_3$	$SiHI_3$
gas	liquid	liquid	red liquid
b.p. −80·2°	b.p. 35°	b.p. 110°	b.p. 220°
m.p. −110°	m.p. −134°	m.p. < −60°	m.p. 8°

The *action of water* on these compounds is various. SiF_4 gives silica gel and hydrofluosilicic acid : $3SiF_4 + 2H_2O = SiO_2 + 2H_2SiF_6$; $SiCl_4$ gives silica gel and hydrochloric acid : $SiCl_4 + 2H_2O = SiO_2 + 4HCl$. Si_2Cl_6 gives silicon-oxalic acid : $Si_2Cl_6 + 4H_2O = (SiO_2H)_2 + 6HCl$. Silicon chloroform gives silico-formic anhydride : $2SiHCl_3 + 3H_2O = (SiOH)_2O + 6HCl$. The reactions of the corresponding bromine and iodine compounds are similar.

Silicon fluorides.—Amorphous and crystalline silicon ignite spontaneously in fluorine, forming gaseous **silicon tetrafluoride** SiF_4. Pure silicon fluoride is obtained by strongly heating barium fluosilicate in a copper tube : $BaSiF_6 = BaF_2 + SiF_4$.

The gas is conveniently prepared by the action of hydrofluoric acid on silica (Scheele, 1771): $SiO_2 + 4HF = SiF_4 + 2H_2O$. Since it is decomposed by water, some dehydrating agent is added. Usually a mixture of equal weights of powdered fluorspar and white sand is heated with concentrated sulphuric acid: $2CaF_2 + 2H_2SO_4 + SiO_2 = 2CaSO_4 + SiF_4 + 2H_2O$. The gas is passed over dry sodium fluoride to free it from hydrofluoric acid, and is collected over mercury. Silicates, such as glass, are decomposed by hydrofluoric acid with formation of silicon fluoride.

Silicon fluoride is a colourless strongly fuming gas, normal density 4·684 g./lit., solidifying without previous liquefaction at -97° at 1 atm. The gas extinguishes a burning taper, but potassium and sodium burn in it when heated: $2SiF_4 + 4K = K_2SiF_6 + 2KF + Si$, and calcium and barium oxides react with incandescence: $SiF_4 + 2CaO = 2CaF_2 + SiO_2$.

Silicon trifluoride Si_2F_6 or $F_3Si{\cdot}SiF_3$ is a colourless inflammable gas formed by the action of the trichloride on zinc fluoride: $Si_2Cl_6 + 3ZnF_2 = Si_2F_6 + 3ZnCl_2$. It is decomposed by water: $Si_2F_6 + 2H_2O = SiO_2 + H_2SiF_6 + H_2$, some silicon-oxalic acid and HF being also formed (Schumb and Gamble, *J.A.C.S.*, 1932, **54**, 583).

Silicon fluoroform $SiHF_3$ is a colourless combustible gas obtained by the action of stannic fluoride or titanium tetrafluoride on silicon chloroform: $4SiHCl_3 + 3SnF_4$ $4SiHF_3 + 3SnCl_4$: it decompose on heating: $4SiHF_3 = 3SiF_4 + 2H_2 + Si$, or in contact with water: $2SiHF_3 + 2H_2O = SiO_2 + H_2SiF_6 + 2H_2$.

Hydrofluosilicic acid.—The reaction between silicon fluoride and water, discovered by Scheele in 1771 but only fully explained by Berzelius in 1823, forms gelatinous silica and a solution of hydrofluosilicic acid:

$$3SiF_4 + 2H_2O = SiO_2 + 2H_2SiF_6.$$

By adding hydrofluoric acid until the silica just dissolves, more hydrofluosilicic acid is formed and the troublesome filtration is avoided:

$$SiO_2 + 6HF = H_2SiF_6 + 2H_2O.$$

The solution of the acid is made technically by percolating aqueous hydrofluoric acid through sand, and as a by-product in superphosphate manufacture (p. 376).

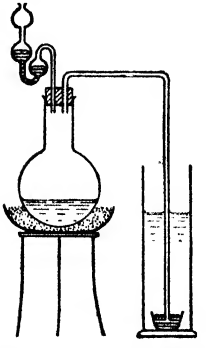


FIG. 232.—Preparation of hydrofluosilicic acid.

EXPT. 2.—Heat on a sand-bath a mixture of 50 g. of powdered fluorspar, 50 g. of fine white sand and 200 c.c. of concentrated sulphuric acid in a stout glass flask with a safety-funnel containing mercury (thin glass is soon perforated) or a stoneware bottle and pass the silicon fluoride into a cylinder, the dry delivery tube dipping under mercury in a small crucible over which water is afterwards poured (Fig. 232). This prevents the tube becoming choked by gelatinous silica, which is deposited in strings of small sacs, each enclosing a bubble of gas; these should be broken occasionally by stirring. The liquid is filtered through linen, and the silica when washed, dried, and heated is very pure (s. g. 2·2).

The anhydrous acid is not known and silicon fluoride and dry hydrogen fluoride do not react.

The acid is partly decomposed in solution (Hudleston and Bassett, *J.C.S.*, 1921, **119**, 403): $H_2SiF_6 \rightleftharpoons SiF_4 + 2HF$, the equilibrium constant at 15° being $[SiF_4][HF]^2/[H_2SiF_6] = 4 \times 10^{-5}$. Crystalline hydrates with 1, 2 and $4H_2O$ have been described.

Pure hydrofluosilicic acid does not corrode glass but on evaporation it decomposes: $H_2SiF_6 \rightleftharpoons SiF_4 + 2HF$ and the hydrofluoric acid formed corrodes a flask or porcelain basin. Jacobson (*J. Phys. Chem.*, 1924, **28**, 506) says the 13·3 p.c. acid distils without decomposition. With steam at high temperatures, crystals of silica are formed.

The salts of hydrofluosilicic acid, the **fluosilicates** (or *silicofluorides*) are formed by careful neutralisation but are decomposed by excess of alkali:

$$H_2SiF_6 + 2NaOH = Na_2SiF_6 + 2H_2O$$
$$Na_2SiF_6 + 4NaOH = 6NaF + SiO_2 + 2H_2O,$$

the end-point with phenolphthalein corresponding with *six* equivalents of base (Wagner and Ross, *Ind. Eng. Chem.*, 1919, **9**, 1116). The dry fluosilicates are best prepared by the action of silicon fluoride gas on the solid fluorides: $SiF_4 + 2NaF = Na_2SiF_6$. The lithium (Li_2SiF_6), calcium ($CaSiF_6$) and strontium ($SrSiF_6$) salts are soluble; Na_2SiF_6, K_2SiF_6, $BaSiF_6$ and rare earth fluosilicates are insoluble and are precipitated by hydrofluosilicic acid. The sodium and potassium salts form nearly transparent gelatinous precipitates, the barium salt a white crystalline precipitate.

Silicon tetrachloride $SiCl_4$ (Berzelius, 1823) is formed by heating amorphous silicon (or a mixture of this with magnesia obtained by heating 40 g. of dry powdered sand and 10 g. of magnesium powder) in a stream of dry chlorine: $Si + 2Cl_2 = SiCl_4$; by passing dry chlorine over heated silicon-iron (Martin, *J.C.S.*, 1914, **105**, 2836), or over an intimate mixture of silica and carbon strongly heated in a porcelain tube (Oersted, 1825): $SiO_2 + 2C + 2Cl_2 = SiCl_4 + 2CO$; or by passing a mixture of dry chlorine and sulphur chloride vapour over red-hot silica (Matignon and Bourion, 1904): $2SiO_2 + S_2Cl_2 + 3Cl_2 = 2SiCl_4 + 2SO_2$. The vapour is condensed in a worm-tube strongly cooled in a freezing mixture and the liquid freed from excess of chlorine by distilling over mercury. It should be kept in a sealed tube.

Silicon tetrachloride is a colourless volatile liquid, s. g. 1·483 at 20°, fuming strongly in moist air: $SiCl_4 + 2H_2O = SiO_2 + 4HCl$, and forming a very dense fume with ammonia.

By the action of chlorine on heated silicon the liquid **trichloride** Si_2Cl_6 and the **octachloride** Si_3Cl_8 are also formed and may be separated by fractionation. The trichloride is also formed by passing the vapour of the tetrachloride over strongly heated silicon. It is a colourless fuming liquid; the hot vapour ignites spontaneously in the air. With water, it produces an explosive white solid **silicon-oxalic acid** $Si_2H_2O_4$ or $(SiO{\cdot}OH)_2$: $Si_2Cl_6 + 4H_2O = (SiO_2H)_2 + 6HCl$, decomposed by dilute alkali: $(SiO{\cdot}OH)_2 + 4KOH = 2K_2SiO_3 + 2H_2O + H_2$. The

octachloride forms with water a white powder $H_2Si_3O_5$ **silicon-meso-oxalic acid**, the structural formula of which has been given as $SiO_2H{\cdot}SiO{\cdot}SiO_2H$. The compounds Si_4Cl_{10}, Si_5Cl_{12} and Si_6Cl_{14} are prepared by the action of a silent discharge on a mixture of $SiCl_4$ vapour and hydrogen, $Si_{10}Cl_{12}$ by the action of heat on this mixture, and $(SiCl)_x$ is also described (Schwarz, etc., 1937–9).

According to Troost and Hautefeuille Si_2Cl_6 vapour begins to decompose at 350° and is completely dissociated at 800°: $2Si_2Cl_6 \rightleftharpoons 3SiCl_4 + Si$. At high temperatures (1000°) reaction begins in the reverse direction and the vapour is stable.

Silicon tetrabromide $SiBr_4$ (liquid) is formed by passing bromine vapour over heated silicon, and **silicon tribromide** Si_2Br_6 (solid) by the action of bromine on Si_2I_6. Si_3Br_8 and Si_4Br_{10} are formed by the action of a silent discharge on $SiHBr_3$.

Silicon tetra-iodide SiI_4 (solid) is formed by passing iodine vapour over heated silicon. When heated with finely divided silver at 280° it forms the solid **tri-iodide** in splendid crystals, fuming in moist air: $2SiI_4 + 2Ag = 2AgI + Si_2I_6$. On heating in vacuum the tri-iodide forms an orange-coloured solid **di-iodide** decomposed by alkali: $Si_2I_4 + 8KOH = 2K_2SiO_3 + 4KI + 2H_2O + 2H_2$.

On passing a mixture of 2 vols. of chlorine and 1 vol. of oxygen over crystalline silicon heated to dull redness several **silicon oxychlorides** are formed (Schumb and Holloway, *J.A.C.S.*, 1941, **63**, 2753), all except Si_2OCl_6 belonging to the homologous series $Si_nO_{n-1}Cl_{2n+2}$:

Si_2OCl_6, b.p. 137°, m.p. −28·1°.	$Si_5O_4Cl_{12}$, b.p. 130°–131°/15 mm.
$Si_3O_2Cl_8$, b.p. 76°/15 mm., m.p. −70°.	$Si_6O_5Cl_{14}$, b.p. 139°–141°/15 mm.
$(SiOCl_2)_4$, b.p. 91°/15 mm., m.p. 77°.	$Si_7O_6Cl_{16}$, b.p. 145°–147°/15 mm.
$Si_4O_3Cl_{10}$, b.p. 109°–110°/15 mm.	

$(SiOCl_2)_4$ is a colourless crystalline solid, the rest are colourless oily liquids hydrolysed by moisture. The last four form glassy solids on cooling in liquid air and have no definite m.ps. The **oxybromides** Si_2OBr_6 and $(SiOBr_2)_4$ are known (Schumb and Klein, *J.A.C.S.*, 1937, **59**, 261).

Silicon chloroform $SiHCl_3$ is prepared by passing hydrogen chloride gas over silicon (or the mixture of silicon and magnesia, p. 509) at a dull red heat (Buff and Wöhler, 1857): $Si + 3HCl = SiHCl_3 + H_2$. The liquid condensed in a freezing mixture is fractionated to separate silicon tetrachloride. Silicon chloroform is a colourless mobile fuming liquid, s. g. 1·3438/15°, very inflammable and burning with a green-edged flame emitting white fumes of silica. A mixture of the vapour with air or oxygen explodes in contact with a flame. At 800° the vapour decomposes into Si, H_2, HCl, $SiCl_4$, and a trace of less volatile liquid: $4SiHCl_3 \rightleftharpoons Si + 3SiCl_4 + 2H_2$.

By the action of ice-cold water on silicon chloroform **silicoformic anhydride** $H_2Si_2O_3$, a white solid, probably polymerised, is formed (Buff and Wöhler, 1857; Stock and Zeidler, *Ber.*, 1923, **56**, 986):

$$SiHCl_3 + 3H_2O = SiH(OH)_3 + 3HCl$$

$$2SiH(OH)_3 = \begin{matrix} O & & O \\ \diagdown\!\!\diagup & & \diagdown\!\!\diagup \\ Si & -O- & Si \\ H\diagup & & \diagdown H \end{matrix} + 3H_2O.$$

This is a powerful reducing agent: $H_2Si_2O_3 + O_2 = 2SiO_2 + H_2O$ (cf. formic acid $H{\cdot}CO_2H + O = CO_2 + H_2O$). It is readily decomposed by dilute alkalis:

$$H_2Si_2O_3 + H_2O = 2SiO_2 + 2H_2,$$

and on heating decomposes ultimately into silica, silicon and hydrogen:

$$2H_2Si_2O_3 = SiH_4 + 3SiO_2 = Si + 2H_2 + 3SiO_2.$$

Silicon bromoform $SiHBr_3$ is produced from hydrogen bromide and heated silicon, **silicon iodoform** $SiHI_3$ by the action of a mixture of hydrogen iodide and hydrogen on heated silicon.

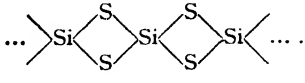
Silicon carbide.—A mixture of sand and crushed coke in the proportions 5 : 3, with a little salt and sawdust, heated electrically to 1550°–2200° by a carbon rod passing through the mass (cf. graphite), forms silicon carbide: $SiO_2 + 3C = SiC + 2CO$, discovered by Acheson in 1891, and manufactured in large quantities at Niagara for use as an abrasive, since it is nearly as hard as diamond. The technical product (*e.g. carborundum*, a trade name) is a black, coarsely crystalline mass exhibiting a play of iridescent colours. It is very difficultly fusible and may be used in furnace-linings; it resists most reagents, but fused caustic soda exposed to air slowly acts upon it: $SiC + 4NaOH + 2O_2 = Na_2CO_3 + Na_2SiO_3 + 2H_2O$. Pure silicon carbide forms transparent, colourless or green, six-sided plates, s. g. 3·1, and is obtained by fusing silicon with carbon in the electric furnace. It has a diamond lattice in which half the carbon atoms are replaced by silicon.

The silicon carbide in the electric furnace is surrounded by a layer of *siloxicon*, said to be a definite compound Si_2OC_2 mixed with a little *silicon monoxide* SiO, but is probably a mixture or solid solution of silica and silicon carbide. It is used as a refractory; a fibrous variety called *fibrox* is used as a heat insulator instead of asbestos.

Silicon borides SiB_3 and SiB_6, which are very hard, are formed in the electric furnace.

Silicon nitrides SiN_2, Si_2N_3 and Si_3N_4 are formed when nitrogen is passed over strongly heated silicon; the nitride $N{\equiv}Si{\cdot}Si{\equiv}N$ is formed by strongly heating the product of interaction of Si_2Cl_6 and ammonia (Schwarz and Sexauer, 1926).

Silicon disulphide SiS_2 is formed in silky needles by heating amorphous silicon in sulphur vapour; it is instantly decomposed by water into hydrogen sulphide and gelatinous silica. It is also formed by passing the vapour of carbon disulphide over a strongly heated mixture of silica and carbon: $SiO_2 + CS_2 + C = SiS_2 + 2CO$. It forms long fibre-like molecules in which SiS_4 tetrahedra are linked by *edges* (Zintl and Loosen, 1935; Büssem, etc., 1935):



Germanium

Germanium was discovered by Winkler in 1886 in a Freiberg mineral *argyrodite* $GeS_2{,}4Ag_2S$ (5 to 7 p.c. Ge). It is found in small amounts in euxenite, some zinc ores, and the ash of some coals (Morgan and Davies, *J.S.C.I.*, 1937, **56**, 717; *Ann. Rep. C.S.*, 1934, 119). One method of extraction depends on the

distillation of the volatile $GeCl_4$ with hydrochloric acid, any gallium in the solution being extracted with ether, but a better process is to extract both gallium and germanium with sodium hydroxide solution: it can be purified by electrodeposition (Sebba and Pugh, *J.C.S.*, 1937, 1371, 1373). The oxide GeO_2 is reduced at a red heat by carbon or hydrogen, and the metal is precipitated by zinc from solutions of its compounds. It is greyish-white, brittle, forms octahedral crystals, and is insoluble in hydrochloric acid but soluble in nitric acid or aqua regia. It does not oxidise in air, but burns when heated in oxygen, chlorine or bromine vapour.

Germanium, like tin, forms two series of compounds, the **germanous compounds** GeX_2 and the better known **germanic compounds** GeX_4.

The **germanium hydrides** resemble those of silicon and are prepared by the action of dilute hydrochloric acid on magnesium germanide Mg_2Ge (made by heating magnesium and germanium in hydrogen) and fractional distillation and condensation in Stock's apparatus (see p. 407; Dennis, etc., *J.A.C.S.*, 1924, **46**, 657; 1925, **47**, 112):

GeH_4	Ge_2H_6	Ge_3H_8
m.p. −165°	m.p. −109°	m.p. −105·6°
b.p. −88°	b.p. 29°	b.p. 110·5°

Monogermane GeH_4 is also prepared by the action of a solution of ammonium bromide in liquid ammonia on Mg_2Ge (Kraus and Carney, *J.A.C.S.*, 1934, **56**, 765): $Mg_2Ge + 4NH_4Br = 2MgBr_2 + GeH_4 + 4NH_3$, and is evolved with hydrogen by the action of dilute sulphuric acid and a germanium compound on zinc (Voegelin, 1902). The germanes decompose on heating into the elements. They are less inflammable than silicon hydrides and are not decomposed by water; GeH_4 is not decomposed by alkali but **digermane** Ge_2H_6 gives hydrogen. Halogen derivatives are formed. Solid yellow $(GeH_2)_x$ is formed by the action of hydrochloric acid on CaGe; on heating it decomposes into hydrogen and gaseous hydrides and when dry reacts explosively with oxygen, forming germanium and water.

Germanic oxide GeO_2 is white and crystallises in two forms, one (s. g. 4·28) isomorphous with quartz and the other (s. g. 6·26) isomorphous with cassiterite (SnO_2). It is non-volatile at the m.p. 1050°, sparingly soluble in water but soluble in hydrochloric acid, forming $GeCl_4$, and in alkali forming a **germanate**, *e.g.* Na_2GeO_3, $Na_2Ge_2O_5$ and $Na_2Ge_4O_9$. The hydroxide is not known and alkalis do not precipitate germanic salts. **Pergermanates** $Na_2GeO_5,4H_2O$ and $Na_2Ge_2O_7,4H_2O$ are formed from hydrogen peroxide and germanates (Schwarz and Giese, 1930).

Germanic fluoride GeF_4 is a colourless fuming gas prepared similarly to SiF_4 and forming H_2GeF_6 with water. The **fluogermanate** ion GeF_6'' is octahedral (Hoard and Vincent, *J.A.C.S.*, 1939, **61**, 2849; 1940, **62**, 3126). **Germanic chloride** $GeCl_4$ is a colourless fuming liquid, b.p. 86°, formed by heating germanium in chlorine, or the metal or GeS_2 with mercuric chloride. It is hydrolysed by water but distils from concentrated hydrochloric acid. By passing a mixture of the vapour and oxygen over quartz at 650° a liquid **oxychloride** Ge_2OCl_6, b.p. 70°/13 mm., is formed, decomposing on boiling at atm. pressure into $GeCl_4$ and GeO_2. **Germanic bromide** $GeBr_4$ is a colourless liquid, the **iodide** GeI_4 is a red solid dissociating on heating: $GeI_4 \rightleftharpoons GeI_2 + I_2$. **Germanium chloroform** $GeHCl_3$ is a colourless fuming liquid, b.p. 75·2°, formed (with some $GeCl_2$) by passing HCl gas over

heated germanium. **Germanic sulphide** GeS_2 is formed as a white precipitate with H_2S in presence of excess of HCl · it is readily soluble in alkali and ammonium sulphides, forming **thiogermanates**, from which it is reprecipitated by a large excess of acid.

Germanous hydroxide $Ge(OH)_2$ or HGeO(OH) is formed as a yellowish-red precipitate by the action of alkali on germanium chloroform :

$$GeHCl_3 + 3NaOH = Ge(OH)_2 + H_2O + 3NaCl ;$$

on heating it forms grey **germanous oxide** GeO. The hydroxide dissolves in alkali to form a **germanite**, *e.g.* Na_2GeO_2 or HGeO·ONa. Reddish-brown **germanous sulphide** GeS is formed by heating GeS_2 in hydrogen : on further heating it forms germanium.

The similarity of germanous and germanic compounds to stannous and stannic compounds is evident. Unlike tin, however, germanium forms only covalent compounds ; there are some stannous salts and salts of bivalent lead are common.

Tin

Some Egyptian hieroglyphics and the word *bedil* in the Old Testament may refer to tin, specimens of which at least as old as 1400 B.C. were found in Egypt. Tin is named κασσίτερος by Homer, and Pliny distinguishes *plumbum nigrum* (lead) from *plumbum candidum* (tin), saying that the latter was brought from the Islands of Cassiterides in the Atlantic, supposed to be the British Isles. The island Iktis on the coast of Britain which (according to Diodorus Siculus) was separated from the mainland only at high water, is identified with St. Michael's Mount, Cornwall. The metal was afterwards called *stannum* (hence the symbol Sn).

Small amounts of *native tin* have been reported in Siberia, Guiana and Bolivia, and in grains with platinum in New South Wales. The ore *stannite* (*tin pyrites*) Cu_2FeSnS_4 occurs in small amounts in Cornwall, Potosi and Bolivia, but the only important source of tin is *tinstone* or *cassiterite* SnO_2 (m.p. 1127°), found in Cornwall, the islands of Banca and Singkep (Dutch East Indies), the Malay Peninsula and Burma, Nigeria and the Belgian Congo, Bolivia, China (Yunnan) and Australia. Tin is one of the rarer metals and is found only in a few places.

Tinstone occurs either in lodes (or veins) or alluvial (*stream tin*) and crystallises in tetragonal prisms terminated by pyramids. It is dense (s. g. 6·95) and is easily separated from lighter rocks by washing. Wolframite ($FeWO_4$) cannot be separated in this way, since its density is 7·1, but is removed by electromagnetic separation or, after roasting, by heating with sodium carbonate at 600°, when soluble sodium tungstate is formed.

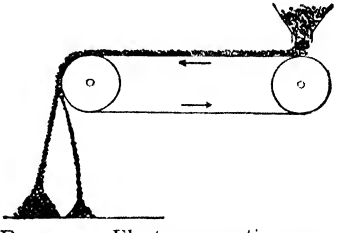


FIG. 233.—Electromagnetic separation (diagrammatic).

In **electromagnetic separation** the crushed ore is carried by a travelling belt passing over a magnetic roller, when it is separated into parts, the magnetic part being pulled towards the roller (Fig. 233). Other forms of apparatus are also used.

The " tin concentrates," containing iron and copper pyrites and arsenical pyrites, are first roasted in an inclined revolving tube-furnace (Oxland and Hocking's calciner), when sulphur and arsenic are expelled as sulphur dioxide and arsenic trioxide, the latter being condensed in chambers for sale. The calcined ore is cooled and soaked in water to dissolve copper sulphate and wash away ferric oxide and light matter. The treated ore (*black tin*) containing 60–70 p.c. of tin as oxide is mixed with one-fifth of its weight of ground anthracite and some lime or fluorspar to form a slag, and smelted at 1200°–1300° in a reverberatory or a shaft furnace (" Cornish tin-castle "): $SnO_2 + 2C = Sn + 2CO$. The slag contains much tin and is smelted with coke in a blast furnace.

The tin bars are heated on the hearth of a reverberatory furnace, when the easily fusible tin (m.p. 232°) flows away, leaving an alloy of tin with copper, iron and arsenic. The tin is then fused and " poled " with billets of green wood (p. 328), when the remaining impurities separate as a scum and tin of over 99 p.c. purity is obtained. The scum and dross are worked up by smelting. The tin must be at least 99·75 p.c. purity to register as " Standard Class A " on the London Metal Exchange; Banca, Billiton and Penang tin is 99·90–99·97 p.c. pure. Electrolytic refining in acid (stannous sulphate or fluosilicate) or alkaline (thiostannate) baths is also used.

Tin has a bright white colour and after fusion a s. g. of 7·29. At 200° it becomes brittle and can be broken by a hammer, forming *grain tin*. On slow cooling of fused tin tetragonal crystals separate. The metal is not very ductile and is too soft to be drawn, but it is very malleable and can be beaten into foil, when the crystalline structure is destroyed. A rod of tin emits a creaking sound (" cry of tin ") when bent: the phenomenon, also shown by zinc and cadmium, seems to be due to a mechanical twinning of the crystals. Tin has a low m.p. but a high b.p. (2260°). Its lustre is not impaired by exposure to air or water, separately or conjointly, and tin is used for tinning iron or copper, with which it readily alloys, forming Fe_2Sn, FeSn, $FeSn_2$, and Cu_3Sn.

Tinplate is made by dipping sheets of iron (given a bright surface in dilute sulphuric acid) into molten tin covered with melted palm oil. The sheet then passes under a partition into molten tin covered with melted fat, and then through rollers to remove superfluous metal. Electroplating from acid or alkaline baths is also used.

Tin is recovered from scrap tinplate, which is washed with alkali to remove grease, rinsed and dried, and treated with chlorine gas in iron cylinders, kept cool. Volatile stannic chloride is formed, and the residue of iron scrap containing less than 0·1 p.c. of tin is hydraulically pressed into blocks and smelted.

When ordinary **white tin** is strongly cooled, it slowly crumbles to a grey powder of s. g. 5·8. The transformation is quickest at −50°. **Grey tin** is an enantiotropic form and the transition point is 13·2°. White tin is metastable under ordinary atmospheric conditions; transformation occurs more easily in contact with a little grey tin (Cohen, 1899; *J.S.C.I.*, 1929, **48**, 162R). Grey tin crystallises (like diamond and silicon) in the regular system. Both white and grey tin are diamagnetic.

Tin is precipitated from a solution of a stannous salt by zinc, iron or aluminium; a piece of zinc suspended in the solution deposits a bright crystalline "tree" and large crystals are formed by adding a suspension of zinc dust to stannous chloride solution.

Tin forms important alloys, *e.g. bronze* (p. 330). A mixture of 1 part of lead and 2 of tin is ordinary *fine-solder* (*soft-solder* consists of equal parts of tin and lead, cheap solder is 7 lead and 3 tin). *Pewter* formerly contained 4 parts of tin and 1 of lead, usually with a little antimony, but modern pewter and *Britannia metal* consist of tin, antimony and copper, with a little bismuth. *Phosphor tin* is a white metallic coarsely crystalline mass, m.p. 370°, formed by adding phosphorus to molten tin.

Tin oxidises when fused in air to a grey scum or dross of a mixture of tin dioxide and unchanged tin: on heating in air this forms tin dioxide, yellow when hot but becoming white on cooling. At a white heat tin burns in air with a white flame and when very strongly heated it decomposes steam: $Sn + 2H_2O = SnO_2 + 2H_2$.

Tin is only slowly attacked by dilute hydrochloric and nitric acids, but readily dissolves in hot concentrated hydrochloric acid, forming stannous chloride: $Sn + 2HCl = SnCl_2 + H_2$. Hot concentrated sulphuric acid gives stannous sulphate and sulphur dioxide with some sulphur, as with zinc: $Sn + 2H_2SO_4 = SnSO_4 + SO_2 + 2H_2O$.

Concentrated nitric acid free from water often has no action on tin, but in presence of a trace of water it acts violently, forming red fumes, a small quantity of soluble tin salt, and an abundant white powder of metastannic acid $H_2Sn_5O_{11}$. Aqua regia readily dissolves tin, forming stannic chloride. Tin is not acted upon by hot concentrated alkalis.

Tin Compounds

Tin forms two series of compounds, the **stannous compounds** SnX_2 of bivalent tin and the **stannic compounds** SnX_4 of quadrivalent tin. Stannous compounds are easily oxidised to stannic compounds and are reducing agents.

Stannous chloride solution gives with mercuric chloride first a white precipitate of mercurous chloride, and in excess a grey precipitate of mercury:

$$SnCl_2 + 2HgCl_2 = Hg_2Cl_2 + SnCl_4$$
$$SnCl_2 + Hg_2Cl_2 = 2Hg + SnCl_4,$$

and when added to a mixture of solutions of a ferric salt and ferricyanide gives a precipitate of Prussian blue, owing to reduction of the ferric salt:

$$2Fe''' + Sn'' = 2Fe'' + Sn''''.$$

Stannous oxide SnO is more basic than stannic oxide SnO_2, but both show feebly acidic properties, forming **stannites** and **stannates**, respectively, in alkaline solution, but both are largely hydrolysed. Stannous salts give the **stannous ion** Sn'', but readily form complex ions such as $SnCl_4''$. Stannic compounds are mostly covalent, and the simple ion Sn'''' probably does not exist; the complex

ions of quadrivalent tin, *e.g.* $SnCl_6''$, however, are quite stable. The coordination numbers of bivalent and quadrivalent tin are 4 and 6, respectively, and many complex compounds corresponding with these are known.

Stannous Compounds

Tinfoil or granulated tin readily dissolves in hot concentrated hydrochloric acid to form a solution of **stannous chloride**: $Sn + 2HCl = SnCl_2 + H_2$, which on evaporation deposits transparent monoclinic prisms of $SnCl_2,2H_2O$, m.p. 40°. They may be dehydrated by heating in vacuum; at atmospheric pressure some hydrochloric acid is lost and a basic salt formed, although at a red heat anhydrous stannous chloride ("butter of tin") distils. The anhydrous salt crystallises from a solution of the hydrate in hot acetic anhydride, but is best prepared, as a transparent glass, by passing dry hydrogen chloride over heated tin. The crystals are rhombic, m.p. 246°, b.p. 603° (or 623°), the vapour being associated: $Sn_2Cl_4 \rightleftharpoons 2SnCl_2$. The fused salt is an electrolyte. Anhydrous stannous chloride is soluble in alcohol and ether; the formula in urethane solution is $SnCl_2$.

The crystals of $SnCl_2,2H_2O$ (*tin salt*) give a clear solution only with a small amount of water (they dissolve in 0·37 parts at 15°) or in presence of hydrochloric acid. With much water white **stannous oxychloride** $2Sn(OH)Cl,H_2O$ or $Sn_2OCl_2,2H_2O$ is deposited. Unless metallic tin is added the acid solution quickly becomes turbid from oxidation, stannous oxychloride being deposited and stannic chloride remaining in solution: $6SnCl_2 + 2H_2O + O_2 = 2SnCl_4 + 4Sn(OH)Cl$. With concentrated hydrochloric acid crystalline **chlorostannous acid** $HSnCl_3,3H_2O$ (m.p. −27°) and in solution H_2SnCl_4 are formed. These correspond with the stable crystalline **chlorostannites**, *e.g.* $KSnCl_3,H_2O$, $K_2SnCl_4,2H_2O$ and $(NH_4)_2SnCl_4,2H_2O$. Compounds of $SnCl_2$ with $\frac{2}{3}$, 1, 2, $2\frac{1}{2}$, 4 and 9 NH_3 are known (Biltz and Fischer, 1923).

Stannous fluoride SnF_2 crystallises (monoclinic) from a solution of stannous oxide in hydrofluoric acid; it is very soluble. **Stannous bromide** $SnBr_2$, rhombic, m.p. 215·5°, b.p. 619°, is light yellow; it is prepared in the same way as the chloride and forms bromostannites.

Stannous iodide SnI_2 is red, monoclinic, m.p. 316°, b.p. 720°; $SnI_2,2H_2O$ crystallises from a solution of stannous chloride and potassium iodide. It is sparingly soluble in water but dissolves in hydriodic acid, forming **iodostannous acid** $HSnI_3$, salts of which are known. **Stannous chloroiodide** SnICl is known.

Basic stannous carbonate $SnCO_3,SnO$ is precipitated as a crystalline powder by adding solid stannous chloride to concentrated sodium bicarbonate solution in a corked flask, and the double salts $K_2[Sn_2(CO_3)_3],2H_2O$ and $(NH_4)_2[Sn(CO_3)_2],3H_2O$ are similarly deposited from stannous chloride and alkali bicarbonate solutions. All these compounds are decomposed by water (Deville, 1862).

Stannous oxide SnO is an olive-green powder formed on heating stannous hydroxide or stannous oxalate: $SnC_2O_4 = SnO + CO + CO_2$ out of contact with air. On heating in air it smoulders and forms stannic oxide. Alkali hydroxide solution precipitates from stannous chloride solution white **hydrated stannous oxide**

$3SnO,2H_2O$, or $2SnO,H_2O$ (Bury and Partington, *J.C.S.*, 1922, **121**, 1998; Weiser and Middleton, *J. Phys. Chem.*, 1932, **36** 3039). In contact with water it slowly forms black crystalline (tetragonal) SnO. Red SnO forms on evaporating to dryness a suspension of stannous hydroxide in NH_4Cl solution. Stannous hydroxide dissolves in dilute acids to form stannous salts and in alkali to form **stannites**, *e.g.* Na_2SnO_2, which are strong reducing agents. The stannite solutions, especially when concentrated, deposit black stannous oxide. Very concentrated alkali decomposes stannous hydroxide to a stannate solution and spongy tin : $2SnO + 2NaOH = Sn + Na_2SnO_3 + H_2O$.

Anhydrous stannous chloride in liquid ammonia is converted by potassamide into SnNK, which reacts with ammonium bromide to form brown amorphous **stannous imide** SnNH : $SnNK + NH_4Br = SnNH + KBr + NH_3$. At 340° in vacuum this forms **stannous nitride** Sn_3N_2, only slightly attacked by hot hydrochloric acid or alkalis (Bergstrom, *J. Phys. Chem.*, 1928, **32**, 433).

Tin dissolves in nitric acid diluted with 1½–2 vols. of water to form **stannous nitrate** : $4Sn + 10HNO_3 = 4Sn(NO_3)_2 + NH_4NO_3 + 3H_2O$, and on strong cooling crystals of $Sn(NO_3)_2,2OH_2O$ (?) separate. The salt is easily hydrolysed.

Stannous sulphide SnS is formed as a brown precipitate when hydrogen sulphide is passed into an acid solution of stannous chloride, or as a grey crystalline mass on heating tin with sulphur at 900°. It melts at 880° but solidifies again at 1000° and remelts above 1200°. It is a good conductor of electricity. The brown precipitate (black when dry) is soluble in hot concentrated hydrochloric acid (arsenic trisulphide is insoluble) ; it is not dissolved by alkali sulphides free from excess of sulphur, but dissolves readily in the polysulphides, *e.g.* yellow ammonium sulphide, to a **thiostannate**, *e.g.* $(NH_4)_2SnS_3$, from which acids precipitate *stannic* sulphide : $(NH_4)_2SnS_3 + 2HCl = 2NH_4Cl + H_2S + SnS_2$.

A solution of hydrated stannous oxide in dilute sulphuric acid deposits crystals of **stannous sulphate** $SnSO_4$ on evaporation over concentrated sulphuric acid. The pure metal does not dissolve in dilute sulphuric acid but dissolves on heating if a little nitric acid is added, and readily in a mixture of 1 vol. of sulphuric acid, 2 vols. of nitric acid and 3 vols. of water. Double salts $K_2Sn(SO_4)_2$ and $K_2Sn_2(SO_4)_3$ are described.

Stannic Compounds

Although the stannic halides are covalent, a sulphate and nitrate are described and seem to be true salts although they are easily hydrolysed. The covalent character is so pronounced that a gaseous hydride is formed.

Tin hydride SnH_4 is obtained (Paneth, etc., 1919–23) mixed with hydrogen by the action of hydrochloric acid on an alloy of tin and magnesium. The pure compound is prepared by electrolysing a solution of tin sulphate containing 0·5 p.c. of dextrin between platinum electrodes, washing the hydrogen (containing 0·01 p.c. of SnH_4) with water and alkaline lead acetate solution, drying by passing through tubes cooled at −80° to −100°, and condensing in liquid air ; the solid melts at −150°. The liquid is then fractionated at low temperatures. The gas is toxic. It is stable in a glass vessel for some days at room temperature, but

rapidly decomposes in presence of minute traces of tin and in contact with $CaCl_2$ and P_2O_5. It decomposes rapidly and completely above 150°, does not react with dilute alkali, dilute hydrochloric acid, dilute or concentrated nitric acid, copper sulphate or lead acetate, but is absorbed by concentrated sulphuric acid or concentrated alkali, solid alkali, soda-lime, and silver nitrate solution (giving a black precipitate containing tin and silver).

Stannic halides are all formed by the action of excess of halogen on the metal; the chloride is liquid, the rest solid.

	SnF_4	$SnCl_4$	$SnBr_4$	SnI_4
m.p.	sublimes at 705°	−33°	30°	143·5°
b.p.		114·1°	293°	340°
s. g.	4·78	2·234 (15°)	3·340 (35°)	4·696 (11°)
	colourless solid	colourless liquid	rhombic colourless	cubic yellow

Stannic fluoride SnF_4, from stannic chloride and anhydrous hydrofluoric acid (Ruff and Plato, 1904): $SnCl_4 + 4HF = SnF_4 + 4HCl$, forms white deliquescent crystals. **Fluostannates**, *e.g.* K_2SnF_6, are analogous to fluosilicates.

Stannic chloride $SnCl_4$ was obtained by Libavius in 1605 by distilling tin with mercuric chloride: $Sn + 2HgCl_2 = SnCl_4 + 2Hg$, and was called *spiritus fumans Libavii*. Tin reacts with chlorine at room temperature to form stannic chloride, which is so obtained in detinning scrap tinplate (p. 514), and stannic chloride is formed by passing chlorine and sulphur chloride vapour over heated stannic oxide: $2SnO_2 + S_2Cl_2 + 3Cl_2 = 2SnCl_4 + 2SO_2$.

EXPT. 3.—Pack granulated tin into a vertical tube closed below and fitted with a cork carrying a calcium chloride tube and a delivery tube passing to the bottom of the tube containing the tin. Pass in dry chlorine slowly, cooling when necessary, until nearly all the tin is converted into stannic chloride. Distil the liquid in a dry flask and condenser and seal in a tube (Lorenz, 1895).

Stannic chloride is a colourless, mobile, strongly fuming liquid which is a non-electrolyte and a poor solvent. The vapour density corresponds with $SnCl_4$. It dissolves in a small quantity of water with evolution of heat and from the clear solution white crystalline hydrates of $SnCl_4$ with 3, 5 and $8H_2O$ can be obtained. The solution also contains unchanged $SnCl_4$, volatile in steam. The hydrate $SnCl_4,5H_2O$ prepared in commerce is called "oxymuriate of tin" or "butter of tin" (a name also used for *anhydrous* $SnCl_2$). This hydrate is used as a mordant and in "weighting" silk. By treating $SnCl_4,5H_2O$ with hydrogen chloride gas at 28° and cooling at 0°, crystals of **chlorostannic acid** $H_2SnCl_6,6H_2O$ are formed, melting at 20°. Stannic chloride combines with alkali chlorides to form **chlorostannates**, *e.g.* $(NH_4)_2SnCl_6$ which crystallises anhydrous, is isomorphous with $(NH_4)_2PtCl_6$, and was used as a mordant in dyeing pink (hence it was called "pink salt") until superseded by $SnCl_4,5H_2O$. The compound $SnCl_4,4NH_3$, formed directly, can be sublimed and dissolves in water without decomposition; $SnCl_4,2SCl_4$, $SnCl_4,2NOCl$, and $SnCl_4,2N_4S_4$ are also formed directly.

The complex acid $H_2SnBr_6,8H_2O$ and salts are known. The corresponding H_2SnI_6 is not known and its salts are not very stable, although Rb_2SnI_6 and Cs_2SnI_6 are known.

Stannic oxide SnO_2 occurs as tinstone or *cassiterite* (tetragonal). It is formed as a white powder by heating tin in air or by the action of nitric acid on tin and heating. The soft white amorphous powder is used (as " putty powder ") for polishing and for making opaque white enamels and glazes. When heated in hydrogen chloride gas it becomes crystalline. A gelatinous hydrated form separates, owing to hydrolysis, on heating a solution of stannic chloride ; when digested with potassium sulphate solution it becomes granular and filters easily.

Stannic acids.—Stannic oxide is acidic and forms **stannates** when fused with alkalis. The ignited dioxide or native tinstone is insoluble in acids (except hot concentrated sulphuric acid) and in alkali solutions, but when fused with sodium hydroxide, and the mass extracted with hot water and crystallised, **sodium stannate** $Na_2SnO_3,3H_2O$ is formed ; it is used as a mordant. It may be regarded as a salt of **metastannic acid** H_2SnO_3 or $O{=}Sn(OH)_2$; orthostannates derived from **orthostannic acid** H_4SnO_4 or $Sn(OH)_4$ are uncommon, but the green cobalt salt Co_2SnO_4 is obtained by heating cobalt and stannic oxides with a flux (Hedvall, 1914).

Potassium amd sodium stannates, $K_2SnO_3,3H_2O$ and $Na_2SnO_3,3H_2O$, have been regarded as $K_2[Sn(OH)_6]$ and $Na_2[Sn(OH)_6]$, analogous to the chlorostannates K_2SnCl_6, etc., as the water cannot be removed without decomposing the salt. They are also isomorphous with the platinates $K_2[Pt(OH)_6]$, etc. (Bellucci and Parravano, 1905). There are hydrates of $K_2Sn(OH)_6$ with 1 and $2H_2O$ and of $Na_2Sn(OH)_6$ with $1H_2O$.

Hydrated stannic oxide appears in two forms, first described by Berzelius in 1817 and regarded by him as isomeric :

a- or **α-stannic acid** is precipitated from stannic chloride solution by ammonia or from a stannate solution by dilute acid. It is soluble in nitric, hydrochloric and dilute sulphuric acids and the solutions do not gelatinise on boiling. The solution in dilute hydrochloric acid is identical with a solution of stannic chloride ; on standing it slowly deposits the second form.

b- or **β-stannic acid** is formed as a curdy white solid by the action of fairly concentrated nitric acid on tin. It is insoluble in nitric acid and concentrated sulphuric acid but concentrated hydrochloric acid converts it into a substance soluble in water, the solution gelatinising on boiling. β-stannic acid removes phosphoric acid almost quantitatively from solutions and may be used for phosphate separation in qualitative analysis, but it is not very satisfactory. β-stannic acid is a weaker acid than α-stannic acid.

Both α- and β-stannic acids are soluble in alkali hydroxide and carbonate solutions and are reprecipitated by acids with their original properties. Boiling concentrated sulphuric acid dissolves β-stannic acid and when the cooled solution is poured into water α-stannic acid is precipitated. On fusing β-stannic acid with alkali an α-stannate is formed.

α-stannic acid when dried at 100° has the composition H_2SnO_3 ; β-stannic acid when dried in vacuum was found by Fremy (1848) to contain 11·3 p.c. of water,

and from this and the composition of the salts he adopted the formula $(H_2SnO_3)_5$, *i.e.* $H_2Sn_5O_{11},4H_2O$, and called it **metastannic acid.*** Cold solutions of alkalis form sparingly soluble **metastannates**, *e.g.* $Na_2Sn_5O_{11},4H_2O$, a crystalline powder, from which acids reprecipitate β-stannic acid.

Engel (1897) by the action of concentrated hydrochloric acid on β-stannic acid obtained a gelatinous mass, partly soluble in water. The filtrate gives with hydrochloric acid a white precipitate which on drying in vacuum forms a glass of the composition $Sn_5O_9Cl_2,4H_2O$, soluble in dilute hydrochloric acid, but reprecipitated by the concentrated acid. It is called **β-stannyl chloride** or **metastannyl chloride.** On boiling or adding sulphuric acid to the solution β-stannic acid $Sn_5O_9(OH)_2,4H_2O$ is quickly precipitated. The white powder obtained by the action of concentrated nitric acid on tin may be the corresponding nitrate, $Sn_5O_9(NO_3)_2,4H_2O$.

If β-stannic acid is heated with water at 100°, it passes according to Engel into **parastannic acid,** $H_2Sn_5O_{11},2H_2O$, which with hydrochloric acid forms a chloride $Sn_5O_9Cl_2,2H_2O$. Kleinschmidt (1918) was unable to prepare parastannic acid. Engel's results may be summarised as follows :

Acid	Dried in air	Dried at 100°	K salt	Chloride
Orthostannic	H_4SnO_4	H_2SnO_3	K_2SnO_3	$SnCl_4$
Metastannic	$H_2Sn_5O_{11},9H_2O$	$H_2Sn_5O_{11},4H_2O$	$K_2Sn_5O_{11},4H_2O$	$Sn_5O_9Cl_2,4H_2O$
Parastannic	$H_2Sn_5O_{11},7H_2O$	$H_2Sn_5O_{11},2H_2O$	$K_2Sn_5O_{11},2H_2O$	$Sn_5O_9Cl_2,2H_2O$

Mecklenburg (1909–14), who prepared specimens of β-stannic acid by heating a dilute solution of stannic sulphate or precipitating it with potassium sulphate, found the water content variable, and concluded that the supposed α- and β-stannic acids are colloidal hydrated stannic oxide with particles of different sizes, those of β-stannic acid being larger. The X-ray patterns of both are identical with that of natural cassiterite or SnO_2 (Weiser and Milligan, *J. Phys. Chem.*, 1936, **40**, 1).

The different chemical properties are difficult to explain on this basis. Thiessen and Körner (*Z. anorg. Chem.*, 1931, **195**, 83) found six breaks in the dehydration curves of hydrated stannic oxide corresponding with $\frac{5}{2}$, 2, $\frac{7}{4}$, $\frac{3}{2}$, 1 and $\frac{1}{2}H_2O$ for 1 molecule of SnO_2.

Colloidal α-stannic acid is formed by dialysing a mixture of stannic chloride solution and alkali, or sodium stannate and hydrochloric acid. As electrolytes pass out the gel first produced gradually forms a clear solution in the dialyser. On heating the sol **colloidal β-stannic acid** is formed.

Perstannic acid corresponds with the unknown *peroxide* SnO_3. By grinding stannic hydroxide with 30 p.c. H_2O_2 at 70° and drying the residue, $HSnO_4,2H_2O$ is obtained ; if dried at 100° $H_2Sn_2O_7,3H_2O$ is formed. By treating a stannate in the same way, **perstannates,** *e.g.* $KSnO_4,2H_2O$ are formed (Tanatar, 1905).

Stannic nitrate $Sn(NO_3)_4$ was said by Berzelius to crystallise from a solution of hydrated stannic oxide in nitric acid. It is said to be formed by the action of 70 p.c. nitric acid on tin and can be quickly separated, but usually hydrolyses to metastannic acid and its existence is doubtful (cf. Walker, *J.C.S.*, 1893, **63**, 845).

* This name, as stated above, should really be given to the acid of simple formula H_2SnO_3.

Stannic sulphide is formed by precipitating a solution of a stannic salt with H_2S. The precipitate is light yellow but becomes black on drying; it is a mixture of tin dioxide and disulphide. Crystalline SnS_2 is obtained as a residue of golden-yellow glistening hexagonal scales (s. g. 4·425), called *mosaic gold*, by heating a mixture of tin filings, sulphur, and sal ammoniac, as described in a fourteenth-century Naples MS. and by Woulfe (*Phil. Trans.*, 1771, **61**, 114). It is insoluble in acids (except aqua regia) but dissolves in alkalis, forming a stannate and thiostannate. Gmelin gave the reactions of formation as:

$$Sn + 4NH_4Cl = (NH_4)_2SnCl_4 + H_2 + 2NH_3$$
$$2(NH_4)_2SnCl_4 + 2S = SnS_2 + (NH_4)_2SnCl_6 + 2NH_4Cl.$$

Sodium orthothiostannate $Na_4SnS_4,18H_2O$ is formed from sodium stannate solution and sodium sulphide. From a solution of it boiled with precipitated SnS_2 the **metathiostannate** $Na_2SnS_3,8H_2O$ crystallises at room temperature. The metathiostannate is also formed by boiling tin and sulphur with a solution of sodium sulphide (Jelley, *J.C.S.*, 1933, 1580; 1934, 1076).

Stannic sulphate is formed in deliquescent crystals $Sn(SO_4)_2,2H_2O$ by evaporating a solution of hydrated stannic oxide in dilute sulphuric acid (1 : 8) to half its volume and cooling.

Lead

Lead is easily reduced from its ores and was known in ancient Babylonia and Egypt; it occurs in early bronzes and a small lead statue of 3000 B.C. Lead is mentioned in Job xix; it was confused with tin but has a separate name (μόλιβος) in Homer and the difference was recognised by Pliny (p. 513). The Greeks obtained it from the Laurion mines but made little use of it. The Romans obtained it from Spain, Gaul and Britain, and used it largely for cisterns, water pipes, etc. There is Roman lead at Bath.

Lead is widely distributed; traces are said to occur native, *e.g.* in Sweden, but the chief ore is *galena*, PbS (s. g. 7·5), with a bright lustre and found *e.g.* in many parts of the United Kingdom, and largely in the U.S.A., Canada, Mexico and Australia. It is generally associated with zinc blende and gangue (quartz, calcite, fluorite, and barytes), and usually contains 0·01–0·1 p.c. of silver. The oxides PbO *lead ochre* and PbO_2 *plattnerite* are rare; the carbonate *cerussite* $PbCO_3$, chlorophosphate *pyromorphite* $3Pb_3(PO_4)_2,PbCl_2$, sulphate *anglesite* $PbSO_4$, sulphatocarbonate *leadhillite* $3PbCO_3,PbSO_4$, and basic sulphate *lanarkite* $PbO,PbSO_4$, are less abundant than galena.

Lead is produced from galena by simple roasting in an oxidising atmosphere; it was smelted in England during the Roman occupation, and smelting in Derbyshire was in active operation in the eighteenth century (Watson, *Chemical Essays*, Cambridge, 1782, **3**, 207, 251).

The galena is separated from gangue and zinc blende by flotation and then smelted. It is first roasted in a reverberatory furnace (Fig. 177) at a moderate temperature, when some is oxidised to oxide and sulphate:

$$2PbS + 3O_2 = 2PbO + 2SO_2$$
$$PbS + 2O_2 = PbSO_4.$$

The temperature is raised, a little quicklime is added, and the remaining lead sulphide reacts with the two oxidised products to form lead :

$$PbS + 2PbO = 3Pb + SO_2$$
$$PbS + PbSO_4 \rightleftharpoons 2Pb + 2SO_2.$$

Except about 10 p.c. passing into the slag all the lead is obtained as metal. The slag is worked up by heating with lime and powdered coal, either in a small blast furnace or on the Scotch hearth, a flat hearth with a *tuyere* for the blast, which has come into use again.

Ore containing silica is roasted either by the *Dwight-Lloyd sinterer*, in which it is heated on a grid and air drawn through, or is mixed with lime and blown in a converter (*Huntington-Heberlein process*) :

$$PbS + 2O_2 = PbSO_4$$
$$PbSO_4 + CaO \rightleftharpoons PbO + CaSO_4$$
$$2CaSO_4 + SiO_2 = Ca_2SiO_4 + 2SO_2 + O_2.$$

The oxidised product is then smelted in a blast furnace with coke and a flux. Sometimes pyrites containing silver and gold, which pass into the lead, are added.

In the *precipitation process*, used in Spain, Germany (the Harz) and America, galena is heated with iron or a material reduced to spongy iron in the smelting process :

$$PbS + Fe = Pb + FeS.$$

Lead is also extracted by *wet processes*. The ore is roasted to sulphate, the soluble sulphates of manganese, magnesium, etc., dissolved out, and the lead sulphate dissolved in saturated brine containing chlorine. Sometimes salt is added during roasting to form $PbCl_2$. The solution is then electrolysed to deposit lead sponge. In some cases the raw ore is agitated with hot brine containing hydrochloric acid, the liquid filtered and the lead chloride deposited on cooling reduced by heating with limestone and coal dust, or by iron.

The crude lead contains copper, antimony and bismuth, which make it hard. It is *softened* by melting on the hearth of a reverberatory furnace until the foreign metals are oxidised and form a scum on the surface, mixed with a little litharge (PbO). It is then desilvered (p. 342). Lead is refined by electrolysis in a solution of lead fluosilicate and H_2SiF_6 with a little gelatin, when a coherent deposit is formed (Betts' process, 1901). Silver, gold and other impurities such as arsenic, antimony, bismuth (a valuable by-product) and copper form an anode slime which is roasted in air to form a gold-silver alloy and oxides of the other metals.

Pure lead has a silver-white lustre, but is usually bluish-grey. It is very soft, dense (s. g. 11·34), and fusible (m.p. 327·4°). The metal boils at 1200° in vacuum, and the vapour is monatomic at 1870°.

Lead crystallises in the cubic system and, like tin, it is diamagnetic. Octahedral crystals separate when the fused metal solidifies, and by precipitation of a solution of lead nitrate or acetate with zinc as a crystalline " tree " : very long and bright " trees " are formed in silica gel (King and Stuart, *J.C.S.*, 1938, 642). Although lead follows tin in the electrochemical series, it is said

to precipitate tin from solutions as neutral as possible. **Colloidal lead** is obtained by Bredig's method (arc between two lead poles under water).

Alloys of lead, besides those with tin (p. 515), are "compo" tubing (lead hardened with 10 p.c. of antimony) and *Frary metal* for bearings, lead with 2 p.c. of barium and 1 p.c. of calcium.

Lead is not attacked by dry air yet it oxidises rapidly but superficially in moist air, a white protective film of basic carbonate being formed. *Pyrophoric lead*, obtained by heating lead tartrate in a tube and sealing off, ignites spontaneously when shaken into air. Lead is not attacked by pure water (except at the boiling point) but slowly decomposes steam at a very high temperature. It rapidly corrodes in water containing dissolved air, a loose deposit of hydroxide, appreciably soluble in water, being formed (Liverseege and Knapp, *J.S.C.I.*, 1920, **39**, 27T).

Lead readily dissolves in warm dilute nitric acid, and in hot concentrated hydrochloric acid it slowly evolves hydrogen. Concentrated sulphuric acid dissolves it rapidly at 230°-240° with evolution of hydrogen and sulphur dioxide, the pure metal being more resistant than the commercial (Barrs, *J.S.C.I.*, 1919, **38**, 407T; Jones, *ibid.*, 1920, **39**, 221, 255T).

Lead is a powerful cumulative poison. A characteristic symptom of lead poisoning, to which painters, plumbers, and potters using lead glazes, are liable, is a blue line on the edges of the gums.

Lead Compounds

Lead forms two series of compounds, the stable **plumbous salts** in which it is bivalent and forms the ion $Pb^{\cdot\cdot}$ in many ways resembling the barium ion $Ba^{\cdot\cdot}$, and the less stable covalent **plumbic compounds** resembling the stannic compounds, in which it is quadrivalent. The plumbic compounds are either insoluble or hydrolysed by water to lead dioxide PbO_2.

What were formerly regarded as plumbous compounds, *e.g.* a *suboxide* said to be formed on heating lead oxalate below 300°: $2PbC_2O_4 = Pb_2O + CO + 3CO_2$, and subhalides PbCl, PbBr and PbI formed from methyl halides and Pb_2O, are apparently mixtures of bivalent compounds and metallic lead (Derbyshire, *J.C.S.*, 1932, 211; Bircumshaw and Harris, *ibid.*, 1939, 1637):

$$3PbC_2O_4 = 2PbO + Pb + 2CO + 4CO_2.$$

Plumbous Compounds

Lead monoxide PbO is formed on heating fused lead in air. The grey dross, a mixture of lead and PbO, roasted in an iron dish, forms a yellow powder of PbO called *massicot*. It darkens on heating, melts at 879° and on cooling breaks up into reddish-yellow scales of *litharge* (Greek *lithos* a stone, *argyros* silver), which is obtained in silver refining (p. 342), and used for making lead salts, red lead, flint glass, paints and varnishes, and in glazing pottery. It is reduced by carbon monoxide at 100°, hydrogen at 310° and carbon at 550°.

There are two crystalline forms of PbO, a yellow rhombic and a red tetragonal, with a transition temperature of 585°. By heating pure lead hydroxide with 15*N* KOH solution near the b.p. square plates of the red form are obtained; 10 *N* KOH solution gives rhombic needles of the yellow form, which comes down black from 3*N* KOH (Applebey and Reid, *J.C.S.*, 1922, **121**, 2129; Moore and Pauling, *J.A.C.S.*, 1941, **63**, 1392).

Plumbous hydroxide $2PbO,H_2O$ or $Pb_2O(OH)_2$ is formed as a white gelatinous precipitate on adding alkali hydroxide to a lead salt solution: it can be obtained in large crystals (Applebey and Reid, *loc. cit.*). $Pb(OH)_2$ is deposited from a plumbite solution on standing (Müller, 1925). The hydroxide loses water at 145°, forming PbO. It is slightly soluble in water (as is PbO, which first forms hydroxide) and the solution turns red litmus blue. It dissolves both in acids and alkalis (except ammonia), forming plumbous salts and **plumbites**, respectively, hence it is amphoteric: $PbO_2'' + 2H^+ \rightleftharpoons Pb(OH)_2 \rightleftharpoons Pb^{++} + 2OH'$. The plumbite solutions are hydrolysed: $PbO_2'' + 2H_2O \rightleftharpoons Pb(OH)_2 + 2OH'$.

PLUMBOUS HALIDES

PbF_2	$PbCl_2$	$PbBr_2$	PbI_2	
m.p. 824°	m.p. 498°	m.p. 366°	m.p. 400°	
b.p. 1290°	b.p. 956°	b.p. 916°	b.p. 954°	All sparingly soluble.
cubic	rhombic	rhombic	hexagonal	
white	white	white	yellow	

Plumbous fluoride PbF_2 is formed as a white precipitate on adding hydrofluoric acid to lead nitrate solution. It is not attacked by chlorine but is decomposed by steam at a bright red heat. The mineral *matlockite* (formerly thought to be an oxychloride) is the **chlorofluoride** PbClF, which is precipitated by a soluble fluoride from lead chloride solution and is used in gravimetric analysis.

Plumbous chloride (*lead chloride*) $PbCl_2$ occurs as *cotunnite* in some volcanic craters; *mendipite* is the oxychloride $PbCl_2,2PbO$. Lead chloride is slowly formed when lead is heated in chlorine or boiled with concentrated hydrochloric acid: $Pb + 2HCl = PbCl_2 + H_2$, but it is usually prepared as a white precipitate by adding hydrochloric acid or a chloride to a solution of a lead salt. It is sparingly soluble (0·91 p.c.) in cold but more soluble (3·2 p.c.) in boiling water; it separates in anhydrous rhombic needles on cooling the hot solution. The vapour density at 1070° corresponds with $PbCl_2$. Lead chloride dissolves in concentrated hydrochloric acid and crystalline complex salts, *e.g.* K_2PbCl_4, KPb_2Cl_5, $NH_4Pb_2Cl_5$ and Tl_3PbCl_5 are known. Compounds of $PbCl_2$ with 1, 2 and 4PbO are known and the white Pb(OH)Cl is called *Pattinson's white lead*. Litharge when boiled with common salt solution reacts (Scheele, 1773): $5PbO + H_2O + 2NaCl \rightleftharpoons 2NaOH + PbCl_2,4PbO$. On heating the residue the yellow **oxychloride** $PbCl_2,4PbO$, used as a pigment and called *Turner's yellow* (1787), is formed. *Cassel yellow* $PbCl_2,7PbO$, made by heating litharge with ammonium chloride, is probably a mixture.

Lead chlorate $Pb(ClO_3)_2,H_2O$, made from litharge and chloric acid, evolves oxygen and chlorine on heating. **Lead perchlorate** $Pb(ClO_4)_2$ forms a violently

explosive solution in methyl alcohol (Willard and Kassner, *J.A.C.S.*, 1930, **52**, 2391).

Lead bromide $PbBr_2$ is formed as a white precipitate. **Lead iodide** PbI_2 is formed as a yellow precipitate (0·06 p.c. dissolves at 15°); on boiling it dissolves (4·34 g./lit.) and separates in golden-yellow spangles on cooling. It is soluble in a large excess of potassium iodide and the solution deposits $KPbI_3,2H_2O$, but is decomposed on dilution.

Lead carbonate $PbCO_3$ is formed as a white crystalline precipitate (s. g. 6·43) on adding a solution of alkali carbonate to a solution of a lead salt in the cold. The precipitate is sparingly soluble in water (0·05 mg./lit.), more soluble (0·14 g./lit.) in water saturated with carbon dioxide, and readily soluble in dilute acetic acid (evolving carbon dioxide) or in ammonium acetate solution. The **basic carbonate** $2PbCO_3,Pb(OH)_2$ is *white lead* (known to Plato as *ψιμύθιον*). Lead carbonate forms rhombic crystals.

Good white lead is *amorphous*, consisting of globules 0·00001–0·00004 in. diameter; it mixes readily with linseed oil and has a great covering-power. *Venetian white* is a mixture of equal parts of white lead and barium sulphate; in *Dutch white* the proportions are one to three.

The so-called *Dutch process* (described by Theophrastos in 300 B.C.) produces the best quality. A roll of lead sheet or a grid of cast lead is placed in an earthenware pot with a perforated shelf and vinegar poured in below. The pots are loosely covered and stacked in rows interstratified with spent tan-bark, the fermentation of which keeps the pots warm and produces carbon dioxide. Basic lead acetate is probably first formed and is then decomposed by the carbon dioxide:

(1) $2Pb + O_2 + 2H_2O = 2Pb(OH)_2$ (in presence of air and moisture).
(2) $Pb(OH)_2 + 2CH_3CO_2H = Pb(CH_3{\cdot}CO_2)_2 + 2H_2O$.
(3) $Pb(CH_3{\cdot}CO_2)_2 + 2Pb(OH)_2 = Pb(CH_3{\cdot}CO_2)_2,2Pb(OH)_2$.
(4) $3[Pb(CH_3{\cdot}CO_2)_2,2Pb(OH)_2] + 4CO_2 = 2[2PbCO_3,Pb(OH)_2] + 3Pb(CH_3{\cdot}CO_2)_2 + 4H_2O$.

The crust of white lead formed in four or five weeks is stripped off, washed, and ground. The moist paste is dried in vacuum ovens.

By boiling litharge with lead acetate solution a basic acetate is formed, which is precipitated by carbon dioxide. The white lead made by this method (*Thenard's process*) is of inferior quality. A good quality is made by a modified *Bischof process* in which carbon dioxide is passed into a suspension of litharge in water.

Lead acetate $Pb(CH_3{\cdot}CO_2)_2,3H_2O$, called *sugar of lead* on account of its sweet taste (it is poisonous), is prepared by dissolving lead oxide (PbO) or carbonate in hot dilute acetic acid, evaporating and crystallising. Excess of lead oxide must not be used, otherwise a sparingly soluble basic salt is formed. By boiling litharge with a solution of lead acetate, a solution of a **basic acetate** called *Goulard's extract* is formed, used as a lotion. Two definite basic acetates are $PbAc_2,Pb(OH)_2$, and $PbAc_2,2Pb(OH)_2$.

Lead nitrate $Pb(NO_3)_2$, discovered by Libavius (*Alchymia*, 1597), deposits in milky-white octahedral crystals, isomorphous with barium nitrate, from a solution of lead, lead oxide or lead carbonate in dilute nitric acid. Clear crystals are deposited from dilute nitric acid. (Excess of lead oxide must not

be used in the preparation, as a basic nitrate is then formed.) Lead nitrate is very soluble in water (38·8 at 0°, 56·5 at 20°, 75·0 at 40° and 138·8 at 100° in g. per 100 g. H_2O). Concentrated nitric acid precipitates it from solution (and also forms a protective coating on lead).

On heating, lead nitrate decrepitates, melts with decomposition at 470° and evolves nitrogen dioxide : the reaction in a sealed tube at 357° is reversible : $2Pb(NO_3)_2 \rightleftharpoons 2PbO + 4NO_2 + O_2$. A **basic nitrate** $Pb(OH)NO_3$ is formed in crystals by boiling a solution of the nitrate with litharge.

Lead orthophosphate $Pb_3(PO_4)_2$ and **pyrophosphate** $Pb_2P_2O_7$ form white precipitates on adding the sodium salts to a solution of lead nitrate or acetate. The orthophosphate dissolves in boiling phosphoric acid and crystals of $PbHPO_4$ separate. The precipitate of $Pb_3(PO_4)_2$ formed from a lead salt and Na_2HPO_4 is converted on long standing in the solution into $PbHPO_4$. $Pb(H_2PO_4)_2$ is formed by dissolving $Pb_3(PO_4)_2$ in 90 p.c. phosphoric acid, evaporating, and washing the crystals with ether (Fairhill, *J.A.C.S.*, 1924, **46**, 1593).

Lead sulphide.—Lead burns in sulphur vapour forming a greyish-black mass of sulphide PbS, which occurs in cubic crystals as *galena*. The sulphide is formed as a black precipitate on passing hydrogen sulphide into a lead salt solution. It dissolves in boiling *dilute* nitric acid with separation of sulphur ; concentrated nitric acid converts it completely into the insoluble sulphate $PbSO_4$. PbS dissolves in hot concentrated hydrochloric acid : $PbS + 2HCl = PbCl_2 + H_2S$. The sulphide melts at 1112° and sublimes in nitrogen from 860°.

H_2S passed into a solution of a lead salt containing excess of hydrochloric acid first forms a yellow or red precipitate of $PbS,PbCl_2$. This afterwards forms black PbS (cf. HgS, p. 401). On diluting a solution of PbS in concentrated hydrochloric acid, $PbS,4PbCl_2$ is precipitated (Lenher, *J.A.C.S*, 1895, **17**, 511 ; 1901, **23**, 680).

Plumbous persulphide $Pb^{II}S_2$ is formed as a dark reddish-brown solid by the action of sulphur on a solution of *s*-butyl lead mercaptan in benzene ; with hydrochloric acid it forms H_2S_2 (Duncan and Ott, *J.A.C.S.*, 1931, **53**, 3940).

Plumbous sulphate (*lead sulphate*) $PbSO_4$ is precipitated by sulphuric acid or a sulphate from a lead salt solution as a heavy white powder, sparingly soluble in water (0·04 g./lit. at 15°) and almost insoluble in dilute sulphuric acid (0·004 g./lit. in 0·5 p.c. acid at 15°). It dissolves in warm ammonium acetate solution, forming feebly ionised lead acetate (Noyes and Whitcomb, *J.A.C.S.*, 1905, **27**, 747 ; Fox, *J.C.S.*, 1909, **95**, 878) or a complex ion $Pb(C_2H_3O_2)^-$ (Sandved and Birnbaum, *J.A.C.S.*, 1940, **62**, 2367). It also dissolves (6 p.c.) in hot concentrated sulphuric acid and deposits in rhombic crystals on cooling ; the compounds $M_2Pb(SO_4)_2$, where M = Na, K and NH_4, are known. With ammonia the **basic sulphate** $PbSO_4,PbO$ is formed, and $PbSO_4,2PbO$ and $PbSO_4,3PbO$ are known.

" Sublimed white lead," a mixture of $75PbSO_4$, 20PbO and 5ZnO, is formed by burning galena containing zinc in an oxidising atmosphere and collecting the fumes.

Plumbic Compounds

Lead hydride PbH_4 was said (Paneth and Nörring, 1920) to be formed by the action of acid on magnesium-lead alloy (in presence of Ra-D, an isotope of lead, a radioactive gas was said to be formed), or by intermittent sparking between a lead oxide-glycerol cement cathode and dilute sulphuric acid with a P.D. of 220 volts. The hydride was condensed by liquid air and on passing the gas through a heated tube a deposit of lead was formed. Pearson and Robinson (*Proc. Roy. Soc.*, 1933, **142**, 275) could not obtain lead hydride, but a volatile hydride is said to be formed by the action of *atomic* hydrogen on lead (Pietsch and Seuferling, 1931).

Lead dioxide ("lead peroxide") PbO_2, discovered by Scheele in 1774, is obtained by boiling red lead with dilute nitric acid, or preferably by the action of cold concentrated nitric acid on red lead, the soluble lead nitrate also formed being washed out with hot water: $Pb_3O_4 + 4HNO_3 = PbO_2 + 2Pb(NO_3)_2 + 2H_2O$. The powder is dried at 100°. Lead dioxide is a chocolate- or puce-coloured powder. It can be obtained in tetragonal crystals.

Lead dioxide is also formed when plumbous compounds are acted upon by powerful oxidising agents in presence of alkalis, *e.g.* in an impure state by adding sodium hypochlorite or bleaching powder solution to a plumbite solution: $PbO + OCl' = PbO_2 + Cl'$. *Pure* lead dioxide is difficult to prepare; it is deposited on the anode on electrolysis of dilute lead nitrate solution with platinum electrodes (Palmaer, *Z. Elektrochem.*, 1923, **29**, 415).

Lead dioxide is a powerful oxidising agent. A mixture with sulphur on trituration burns with a brilliant flame and forms lead sulphide. Lead dioxide becomes red-hot when warmed in a stream of sulphur dioxide: $PbO_2 + SO_2 = PbSO_4$. It inflames hydrogen sulphide and removes ammonium sulphide from solutions on boiling. It dissolves slowly, with evolution of oxygen, in boiling dilute nitric acid. On boiling a solution of a manganous salt with nitric acid and lead dioxide a pink solution of permanganic acid is formed (Crum, 1845):

$$2MnSO_4 + 5PbO_2 + 6HNO_3 = 2HMnO_4 + 2PbSO_4 + 3Pb(NO_3)_2 + 2H_2O,$$

and chromic hydroxide in presence of alkali is oxidised to chromate (Chancel, 1856):

$$2Cr(OH)_3 + 10KOH + 3PbO_2 = 2K_2CrO_4 + 3K_2PbO_2 + 8H_2O.$$

Lead dioxide heated at 350° in air forms Pb_2O_3 and at 440° Pb_3O_4 (Debray, 1878).

Plumbates.—Lead dioxide is acidic and with strong bases forms plumbates, derived from **plumbic acids** (Fremy, 1844), formulated by Bellucci and Parravano (1906) as:

H_4PbO_4	H_2PbO_3	$H_2[Pb(OH)_6]$
$Pb(OH)_4$	$O{=}Pb(OH)_2$	
ortho-	*meta-*	*hexa-*

On adding lead dioxide to 100 g. of potassium hydroxide and 30 g. of water, fused in a silver dish, till no more dissolves, a plumbate is formed. The solution in water containing excess of KOH deposits crystals of **potassium**

plumbate $K_2PbO_3,3H_2O$ or $K_2Pb(OH)_6$ on evaporation in vacuum and seeding with a crystal of the isomorphous stannate. The sodium salt should be formulated $Na_2PbO_3,3H_2O$ and not $Na_2Pb(OH)_6$, since it can be dehydrated at 110° without decomposition (Grube, 1922; Simon, 1928); Na_2PbO_3 on heating decomposes into PbO_2 and Na_2O and at 750° into PbO, Na_2O and oxygen.

Orthoplumbic acid is not known but the calcium salt, which forms a nearly colourless dihydrate $Ca_2PbO_4,2H_2O$, is formed by heating a mixture of litharge and quicklime in air (Kassner, 1890): $2PbO + 4CaO + O_2 = 2Ca_2PbO_4$. When digested with sodium peroxide and water it forms the metaplumbate $CaPbO_3,4H_2O$. At 250° in dry air, Ca_2PbO_4 is said to form a **perplumbate** $CaPb_2O_6$ (Kassner, 1899–1900).

Metaplumbic acid is said to be deposited as a black powder on the anode in the electrolysis of a slightly alkaline solution of lead sodium tartrate, but the product varies in water content (Glasstone, *J.C.S.*, 1922, **121**, 1469). The anodic deposit from alkaline potassium plumbite is said to be plumbous metaplumbate: $Pb^{II}Pb^{IV}O_3,3H_2O$ (Grube, 1922).

Lead sesquioxide Pb_2O_3, which is *plumbous metaplumbate* $Pb^{II}Pb^{IV}O_3$, is obtained as a reddish-yellow powder by adding sodium hypochlorite to a solution of sodium plumbite: $2PbO + NaOCl = Pb_2O_3 + NaCl$; by electrolysis of the plumbite solution; and (as $Pb_2O_3,3H_2O$) by oxidising this solution with bromine water. It is also precipitated on mixing solutions of alkali plumbite and plumbate. It is decomposed by dilute nitric acid into lead dioxide and a plumbous salt: $Pb_2O_3 + 2HNO_3 = PbO_2 + Pb(NO_3)_2 + H_2O$.

An oxide Pb_5O_8 is formed in large crystals by heating PbO_2 with sodium hydroxide solution in a bomb at 295°–310° (Clark, Schieltz and Quirke, *J.A.C.S.*, 1937, **59**, 2305; Gross, *ibid.*, 1941, **63**, 1168); Pb_2O_3 is formed at 260°–275° and Pb_3O_4 at 355°–375°.

Red lead (or *minium*) Pb_3O_4, which is described by Dioskurides (first cent. A.D.), is made by heating massicot (PbO) in air at 450°–470° or white lead at 425°–430°. It is *plumbous orthoplumbate* $Pb_2^{II}(Pb^{IV}O_4)$, as is seen from the reaction with nitric acid, which removes bivalent lead as nitrate and leaves PbO_2, and also from its formation from a plumbous salt and a plumbate in solution. Red lead contains some PbO, which can be removed by washing with 10 p.c. potassium hydroxide, leaving Pb_3O_4 of 99·7 p.c. purity. Red lead is used as an oxidising agent, in making flint glass and for anti-corrosion paint for iron.

Lead tetrafluoride PbF_4 is formed by dissolving red lead or freshly prepared lead dioxide in 96 p.c. hydrofluoric acid. It forms complex salts, Na_2PbF_6, Rb_2PbF_6, Cs_2PbF_6, $PbF_4,3NH_4F,HF$ or $(NH_4)_3HPbF_8$, and $PbF_4,3KF,HF$ or K_3HPbF_8 is formed by fusing lead dioxide with KHF_2, and crystallising the solid from concentrated hydrofluoric acid (Mathers, *J.A.C.S.*, 1920, **42**, 1309).

Lead tetrachloride $PbCl_4$ is contained as the complex **chloroplumbic acid** H_2PbCl_6 in the yellow solution of lead dioxide in cold concentrated hydrochloric acid, into which chlorine may be passed (Millon, 1842). On adding

ammonium chloride a bright yellow precipitate of **ammonium chloroplumbate** $(NH_4)_2PbCl_6$ is formed (Nikoljukin, 1885; Wells, *Amer. Chem. J.*, 1893, **46** 180). When this is added to cold concentrated sulphuric acid the free acid H_2PbCl_6 breaks up at once and yellow fuming liquid **lead tetrachloride** or **plumbic chloride** $PbCl_4$ is deposited (H. Friedrich, *Ber.*, 1893, **26**, 1434). This has a s. g. of 3·18, freezes at −15°, and readily decomposes on warming with evolution of chlorine: $PbCl_4 = PbCl_2 + Cl_2$. At 105° it explodes. It forms a deep red solution in benzene.

On the addition of a *little* water $PbCl_4$ forms a crystalline hydrate, but it is readily hydrolysed, giving a brown precipitate of hydrated lead dioxide. The ion $Pb^{\cdots\cdot}$ (like $Sn^{\cdots\cdot}$) is very unstable; the insoluble dioxide or a complex ion is formed when the ion might be expected: $Pb^{4+} + 3OH^- = PbO_2 + H^+ + H_2O$.

An orange-coloured solution of chloroplumbic acid is formed by electrolysis of concentrated hydrochloric acid with a lead anode (Elbs, 1902–3).

Lead tetra-acetate $Pb(CH_3{\cdot}CO_2)_4$ is the most stable plumbic compound and is deposited in white needles on cooling a solution of red lead (PbO_2 is insoluble) in hot glacial acetic acid. It is decomposed by moisture with formation of brown lead dioxide. It is a good oxidising agent.

By electrolysis of sulphuric acid, s. g. 1·7–1·8, below 30° with a lead anode in a porous pot, **plumbic sulphate** $Pb(SO_4)_2$ is formed in yellow crystals decomposed by water: $PbSO_4 + SO_4 = Pb(SO_4)_2$; $Pb(SO_4)_2 + 2H_2O = PbO_2 + 2H_2SO_4$. It is probably formed in the overcharged lead accumulator.

Titanium

Gregor in 1789 recognised the existence of a new metal in a black sand in Cornwall, now called *ilmenite* or *titaniferous iron ore*, also found in Nova Scotia and New Zealand: it is ferrous titanate $FeTiO_3$. The element was called *titanium* by Klaproth in 1794. Other minerals are *perovskite* $CaTiO_3$, *titanite* (or *sphene*) $CaTiSiO_5$, and the dioxide TiO_2 which occurs in three forms (cf. SiO_2): *rutile*, tetragonal prisms isomorphous with cassiterite SnO_2, s. g. 4·21; *anatase*, slender tetragonal pyramids, s. g. 3·88; and *brookite*, flat rhombic prisms, s. g. 4·17. TiO_2 is very widely distributed in iron ores, silicate rocks, clay, bauxite, coal (up to 2·6 p.c. in ankerite) and soil (average 0·57 p.c.), and most commercial iron contains titanium. Titanium also occurs in small amounts in plant and animal tissues and bones.

Ferrotitanium, made in the electric furnace, is used to remove oxygen and nitrogen from molten steel, and steel containing some titanium has toughness and resistance to wear, *e.g.* as rails. Hydrated titanium dioxide mixed with barium sulphate is used as a pigment (*titanium white*), titanium dioxide is used in tinting artificial teeth and in making a yellow glaze for porcelain, and a solution of the trichloride $TiCl_3$ in dyeing as a mordant and in removing dyes from fabrics.

Titanium dioxide is manufactured from ilmenite by three processes: (i) The *acid process* (used in Norway) in which the powder is heated with concentrated sulphuric acid, the iron and titanium sulphates dissolved in water, and TiO_2 precipitated from the solution by hydrolysis. (ii) The *alkaline process* (used in the U.S.A.) in which the mineral is fused with sodium sulphide and the mass extracted with water; FeS and TiO_2 remain and the FeS is dissolved in a solution of sulphurous acid. (iii) The *chlorine process*, in which a mixture of ilmenite

and carbon is heated in a stream of chlorine at 350° to chlorinate the iron and then at 550°, when volatile $TiCl_4$ distils and is then hydrolysed by water to TiO_2.

Metallic titanium was first obtained impure as a black powder by Berzelius in 1825 by heating potassium fluotitanate K_2TiF_6 with sodium. A purer metal (containing 2 p.c. of carbon) was made by Moissan (1895) by reducing excess of TiO_2 with carbon in the electric furnace and remelting the metal with TiO_2. Pure titanium is difficult to obtain as it readily combines with oxygen, nitrogen, carbon and silicon : most of the early specimens contained carbon and nitrogen, *e.g.* the copper-coloured cubes found in some blast furnaces, which Wöhler (1850) thought consisted of titanium cyano-nitride $Ti(CN)_2,3Ti_3N_2$, are a mixture of the nitride TiN and graphite (Rudge and Arnall, *J.S.C.I.*, 1928, **47**, 376T). The pure metal is obtained by (i) heating liquid $TiCl_4$ with sodium in a closed iron bomb, when so much heat is evolved that the titanium (m.p. 1800°) is partly fused (Nilson and Pettersson, 1887 ; Hunter, *J.A.C.S.*, 1910, **32**, 330) ; (ii) heating TiO_2 and calcium in a vacuous iron vessel (Wedekind, 1913) ; (iii) strongly heating a tungsten filament in TiI_4 vapour (van Arkel and de Boer, 1925). Titanium forms white very hard brittle hexagonal crystals, s. g. 4·50 ; it welds at a red heat. When heated it burns in oxygen and decomposes steam ; it dissolves in cold dilute sulphuric or hot concentrated hydrochloric acid with evolution of hydrogen, forming *titanous* salts (Ti^{+++}). It *burns* in nitrogen at 800°, forming the *nitride* TiN. It forms a hard refractory *carbide* TiC, *silicide* $TiSi_2$ and *boride*.

Titanium forms three series of compounds in which it has valencies of 4, 3 and 2, those of 4-valent titanium being best known and most stable. A tendency to form compounds of the *titanyl* radical =Ti=O is less marked than with zirconium and =Zr=O.

Titanium dioxide can be prepared from rutile (Wöhler, 1849) by fusing with K_2CO_3, dissolving in dilute HF and crystallising K_2TiF_6,H_2O (glittering leaflets) ; from a solution of this in hot water ammonia precipitates white hydrated TiO_2 (*titanic acid*), on heating which TiO_2 is formed as a white powder, yellow when hot. TiO_2 is also formed when K_2TiF_6 is heated with concentrated sulphuric acid (cf. K_2SiF_6, which gives SiF_4). Titanium dioxide dissolves in hot concentrated sulphuric acid to form **titanyl sulphate,** which forms crystals, $TiO(SO_4),2H_2O$. A solution is used as a test for H_2O_2 (p. 679), the yellow or orange colour being due to **pertitanic acid,** which is formed as a bright yellow precipitate on adding H_2O_2 and ammonia to a solution of $TiCl_4$ in alcohol. The old formula is $TiO_3,3H_2O$, but it probably contains 4-valent Ti and is $(HO)_3{=}Ti{-}O{-}OH$ (Melikov and Pissarjevsky, 1898–9) or $(HO)_2{=}Ti{=}O,H_2O_2$ (Schwarz, 1927), although **fluoxypertitanates,** *e.g.* $TiO_2F_2,3NH_4F$ or $(NH_4)_3[TiO_2F_5]$ and similar compounds, may be derived from TiO_3. Titanium dioxide also shows weakly acidic properties, forming *titanates, e.g.* $K_2TiO_3,4H_2O$. These are derived from supposed *titanic acids, e.g.* metatitanic acid H_2TiO_3, precipitated on boiling a solution of titanyl sulphate and acetic acid for some hours (Zr is not precipitated), but the products all show only the X-ray spectrum of TiO_2 as rutile or anatase (Weiser and Milligan, *J. Phys. Chem.*, 1934, **38**, 513).

Titanium tetrafluoride TiF_4 is a white solid, b.p. 284°, prepared by the reaction : $TiCl_4 + 4HF$ (anhyd.) $= TiF_4 + 4HCl$. The complex acid H_2TiF_6 is present in a solution of TiO_2 in aqueous HF and forms crystalline salts M_2TiF_6 isomorphous with Si, Zr and Sn^{IV} compounds.

Titanium tetrachloride $TiCl_4$, m.p. −30°, b.p. 136·4°, is a colourless strongly fuming liquid (used along with ammonia for smoke-screens) prepared by passing

chlorine over heated titanium or a mixture of TiO_2 and carbon, or chlorine or CCl_4 vapour at a high temperature over TiO_2: $2Cl_2 + TiO_2 \rightleftharpoons TiCl_4 + O_2$. It is soluble in water but is hydrolysed by excess, depositing hydrated TiO_2; with NH_4Cl and hydrochloric acid it forms yellow crystals of $(NH_4)_2TiCl_6,2H_2O$.

Titanium tetrabromide $TiBr_4$, an amber-yellow solid, m.p. 39°, b.p. 230°, is formed similarly to $TiCl_4$ or from $TiCl_4$ and HBr. The red solution in hydrobromic acid probably contains H_2TiBr_6, and $(NH_4)_2TiBr_6,2H_2O$ forms red crystals.

Titanium tetra-iodide, m.p. 150°, b.p. 360°, a reddish-brown solid, is formed by heating titanium in iodine vapour or by the reaction $TiCl_4 + 4HI = TiI_4 + 4HCl$. No complex acid H_2TiI_6 or salts are known.

Brown **titanic nitride** Ti_3N_4 is formed by the action of liquid ammonia and KNH_2 on $TiBr_4$ (Ruff and Treidel, 1912): it is decomposed by heat into TiN and nitrogen and by water into TiO_2 and ammonia. **Titanium disulphide** TiS_2 is formed in yellow scales (like SnS_2) by passing $TiCl_4$ vapour and H_2S through a heated tube. Some **double sulphates** of Ti^{IV} are $Ca[Ti(SO_4)_3]$ and $Ba_2[Ti_3(SO_4)_8]$; the simple sulphate is doubtful.

The most important compound of 3-valent titanium is the **trichloride** $TiCl_3$, formed in dark violet scales on passing a mixture of $TiCl_4$ vapour and hydrogen through a heated tube (Ebelmen, 1847). On heating in hydrogen chloride it forms $TiCl_4$: $2TiCl_3 + 2HCl = 2TiCl_4 + H_2$. The solution (which is deep violet when pure but inky black if $TiCl_4$ is present) is formed by reducing a solution of $TiCl_4$ in hydrochloric acid with zinc. It is a powerful reducing agent (*e.g.* reducing perchlorate to chloride).

Two forms of the solid hydrate $TiCl_3,6H_2O$, violet and green, are known (cf. $CrCl_3,6H_2O$). $(NH_4)_3[TiF_6]$, containing 3-valent Ti, is isomorphous with compounds of Cr^{III}, VIII and Fe^{III}. $Rb_2[TiCl_5],H_2O$ and $Cs_2[TiCl_5],H_2O$ are green but form violet solutions. Alkalis precipitate from $TiCl_3$ solution the dark brown or blue hydrated **sesquioxide** Ti_2O_3 or $Ti(OH)_3$; anhydrous Ti_2O_3 (a black powder or red crystals) is formed by heating TiO_2 strongly in dry hydrogen. The bronze-yellow **titanous nitride** TiN is formed from the elements or by heating TiO_2 in ammonia gas at 1400°–1500°(Ruff, 1909). It contains 3-valent titanium Ti≡N, as is shown by dissolving in dilute H_2SO_4 and HF and titrating with $KMnO_4$.

Titanium sesquisulphide Ti_2S_3 is a grey powder formed on passing H_2S and CS_2 vapour over heated TiO_2. **Titanium sesquisulphate** (or **titanous sulphate**) $Ti_2(SO_4)_3,8H_2O$ is said to be formed in violet crystals on evaporating a solution of titanium in dilute sulphuric acid (the product is also described as $TiSO_4$ and $H_2[Ti_6(SO_4)_{10}],25H_2O$; anhydrous $Ti_2(SO_4)_3$ is described as green). Stable violet rubidium and caesium **titanium alums** $MTi(SO_4)_2,12H_2O$ are formed by electrolytic reduction of a solution of TiO_2 and alkali sulphate in sulphuric acid.

Bivalent Ti compounds are known. The black **dichloride** $TiCl_2$ is formed by heating $TiCl_3$ in vacuum at 400°: $2TiCl_3 = TiCl_4 + TiCl_2$, or in hydrogen to bright redness in entire absence of oxygen and moisture (Friedel and Guérin, 1875). It smoulders on heating in air, forming $TiCl_4$ and TiO_2, evolves hydrogen with water and forms a green solution in concentrated hydrochloric acid. The **di-iodide** TiI_2 is formed by heating TiI_4 and mercury vapour. The **monoxide** TiO is formed by heating TiO_2 at a very high temperature, or with carbon or magnesium, or in hydrogen at 2000° at 150 atm., and the **monosulphide** TiS is a red metallic solid formed on strongly heating Ti_2S_3 in hydrogen.

Zirconium

Klaproth in 1789 isolated a new " earth " *zirconia* (ZrO_2) from the mineral *zircon* ($ZrSiO_4$), gem forms of which are *hyacinth* and *jargon*. Zircon, with a resinous lustre like zinc blende, occurs in alluvial sands in Ceylon, the Urals, Australia and North Carolina. *Baddeleyite*, found in Ceylon and Brazil, is the oxide ZrO_2 and is the main source. Large quantities of *zirkite*, a mixture of oxide and silicate, are found at Minas Geraes, Brazil.

Zirconium compounds are made from zircon by fusing with sodium hydroxide and boiling with water, when sodium silicate dissolves and impure ZrO_2 is left. It is dissolved in hydrochloric acid, evaporated to dryness to render silica insoluble, and precipitated with ammonia. Baddeleyite is boiled with concentrated hydrochloric acid to remove impurities, boiled with concentrated sulphuric acid or fused with $NaHSO_4$, the **zirconyl sulphate** $ZrO(SO_4)$ dissolved and precipitated with ammonia and the hydrated ZrO_2 heated, when it glows and forms white infusible zirconia ZrO_2 (m.p. 2700°, b.p. 4300°?), used for refractories and white enamels. It forms tetragonal crystals isomorphous with rutile (TiO_2) and cassiterite (SnO_2). A mixture of ZrO_2 with rare earths (Y_2O_3 and Er_2O_3) forms *Nernst filaments* which conduct electrolytically when hot.

Metallic zirconium, discovered by Berzelius (1824) by heating K_2ZrF_6 with potassium or sodium, is also obtained by heating K_2ZrF_6 with aluminium, $ZrCl_4$ with sodium, ZrO_2 with calcium in vacuum, or very pure by heating a tungsten filament in ZrI_4 vapour (van Arkel and de Boer, 1925–30). It usually forms very hard white scales (cubic), m.p. 1600°, but is soft and malleable when quite pure (Marden and Rich, *Ind. Eng. Chem.*, 1920, **12**, 651 ; de Boer, *ibid.*, 1927, **19**, 1257). It forms a tough, bullet-proof, alloy steel. Zirconium is only slowly attacked by acids except HF and aqua regia. On heating in hydrogen it forms a black **hydride** ZrH_2. Zirconium shows close chemical analogies to silicon. It is predominantly quadrivalent but $Zr^{III}Cl_3$ and $Zr^{II}Cl_2$ (and $ZrBr_3$ and $ZrBr_2$) are known.

Zirconia ZrO_2 is amphoteric and on fusion with alkalis forms *zirconates*, Na_2ZrO_3, etc., but the precipitated hydrated oxide is insoluble in aqueous alkali but soluble in acids. Hydrogen peroxide precipitates zirconium quantitatively as **hydrated peroxide** $(HO)_3Zr—O—OH$, and in presence of alkali and alcohol a **perzirconate** is precipitated.

Zirconium tetrafluoride ZrF_4 is white, monoclinic, can be sublimed, and is not hydrolysed : it is formed by the reaction $ZrCl_4 + 4HF$ (anhyd.) $= ZrF_4 + 4HCl$.

Fluozirconates are K_2ZrF_6 (isomorphous with Si, Ti and Sn^{IV} compounds) and K_3ZrF_7 (containing the ion ZrF_7''' : Hampson and Pauling, *J.A.C.S.*, 1938, **60**, 2702).

Zirconium tetrachloride $ZrCl_4$, white, cubic, subliming at 300°, is formed by passing dry chlorine over a strongly heated mixture of ZrO_2 and carbon, or Cl_2 and CO over ZrO_2 at 480°. The vapour density corresponds with $ZrCl_4$. It is hydrolysed by water, and white needles of $ZrOCl_2,8H_2O$ are formed on evaporating a solution in hydrochloric acid. The white volatile **tetrabromide** $ZrBr_4$ is formed similarly to $ZrCl_4$; the yellow **tetra-iodide** is not formed directly but sublimes on passing HI over strongly heated zirconium, and gives with water $ZrOI_2,8H_2O$.

Zirconium forms amorphous **basic carbonates** of indefinite composition, perhaps including $ZrO(CO_3)$, and is thus more electropositive than titanium.

Zirconium nitrate $Zr(NO_3)_4,5H_2O$ may be a zirconyl compound $(ZrO)H_2(NO_3)_4,4H_2O$, and there is a basic nitrate $ZrO(NO_3)_2,2H_2O$; the commercial salt is indefinitely basic.

Sodium phosphate precipitates **zirconium phosphate** $ZrH_2(PO_4)_2$, insoluble in HCl but soluble in HF (serving to separate Zr from all elements except Hf): on heating it forms ZrP_2O_7. **Zirconium disulphide** ZrS_2, stable to water, is formed by heating $ZrCl_4$ with H_2S or sulphur vapour. **Zirconium sulphate** $Zr(SO_4)_2$ is formed by dissolving ZrO_2 in hot concentrated sulphuric acid, evaporating and heating the residue. It crystallises from water as $ZrO(SO_4),H_2SO_4,3H_2O$, or $H_2[ZrO(SO_4)_2],3H_2O$, which readily loses $3H_2O$. A **basic sulphate** $4ZrO_2,3SO_3,15H_2O$ deposits from dilute solution and $2ZrO_2,3SO_3,5H_2O$ from boiling concentrated solution. The **acid sulphate** $H_2[Zr(SO_4)_3],1$ and $3H_2O$ separates from strongly acid solutions. A neutral zirconium solution gives with potassium sulphate a precipitate of an indefinite basic double sulphate, insoluble in HCl (separation of Zr from Ti, Nb, Ta).

By heating $ZrCl_4$ and aluminium in hydrogen at 300° the brown **trichloride** $ZrCl_3$ is formed and this on heating in vacuum at 350° gives the black **dichloride** $ZrCl_2$: $2ZrCl_3 = ZrCl_2 + ZrCl_4$; they both evolve hydrogen from water. At high temperatures the reactions $2ZrCl_2 = ZrCl_4 + Zr$, $2ZrCl_2 + 2HCl = 2ZrCl_3 + H_2$ and $2ZrCl_3 + 2HCl = 2ZrCl_4 + H_2$, occur. A green **sesquioxide** Zr_2O_3 (by burning ZrH_2 in air) and a black **monoxide** ZrO (by heating ZrO_2 and Mg in H_2) are doubtful. The **nitride** ZrN is refractory.

Hafnium

The element hafnium was discovered in an X-ray examination of zirconium minerals by Coster and Hevesy in 1923 (Hevesy, *J.C.S.*, 1923, **113**, 3218; 1931, 1). It occurs to the extent of about 1 in 100,000 in the earth's crust and in all zirconium minerals, usually 0·1 p.c. or less, although baddeleyite contains 1 to 2 p.c. and zircon up to 7 p.c. *Alvite* (Zr, Hf, Th)SiO_4, and *malacone*, an altered form of zircon (with occluded argon), contain up to 60 p.c. It gives practically all the reactions of zirconium and is found in most commercial zirconium compounds (3 p.c. in ordinary zirconia). It is best separated from zirconium by fractional crystallisation of the double fluorides $(NH_4)_2ZrF_6$ and $(NH_4)_2HfF_6$ (more soluble). The crystal of the double fluoride $(NH_4)_3HfF_7$ contains $(NH_4)_2HfF_6$ and NH_4F units (cf. Zr). The white **metal** (m.p. 2200°, s. g. 13·07), obtained by heating K_2HfF_6 or $HfCl_4$ with sodium, or heating a tungsten filament in HfI_4 vapour (de Boer, 1930), has been added to tungsten lamp filaments. The white **dioxide** HfO_2 (m.p. 2812°) is refractory and is more basic than ZrO_2. The white solid **chloride** $HfCl_4$ is more volatile than $ZrCl_4$ and sublimes at 250°. The **carbide** HfC and double carbide HfC,4TaC have probably the highest m.ps. (over 4000°) of any known substances. Other compounds are the **sulphide** HfS_2, **sulphate** $Hf(SO_4)_2$ decomposing at a higher temperature (500°) than $Zr(SO_4)_2$, and double sulphate $K_2[HfO(SO_4)_2],3H_2O$.

Thorium

Thorium was discovered in the Norwegian mineral *thorite* $ThSiO_4$ by Berzelius in 1828, and as the oxide is a strong base he regarded it as an "earth" and formulated it ThO. The formula ThO_2 was proposed by Delafontaine in 1863 from the isomorphism of thorium compounds with those of tin, titanium

and zirconium. *Thorite* is chiefly $ThSiO_4$ with small amounts of uranium and other metals and contains 60 p.c. of ThO_2; *orangeite* is a yellow form. *Thorianite*, found in Ceylon, and formerly mistaken for pitchblende, is 70 to 80 p.c. free thoria ThO_2 with some uranium, lead and rare earth oxides and 9 c.c. of occluded He per g. The chief source of thorium is *monazite*, a phosphate of cerium and lanthanum (p. 432) with 4 to 18 p.c. of ThO_2 and 1 c.c. of He per g., found as sand in Brazil and at Travancore in India.

Thoria is used for incandescent mantles, mixed with 1 p.c. of CeO_2 (pure ThO_2 gives a feeble light) and is extracted from monazite. This is heated with concentrated sulphuric acid, thorium phosphate precipitated by magnesia, heated with sodium carbonate to form thoria, and this purified by a process depending on the solubility of thorium oxalate in ammonium oxalate solution (cerium and lanthanum oxalates are only very sparingly soluble). On heating the oxalate thoria is formed and by dissolving in nitric acid the crystalline **thorium nitrate** $Th(NO_3)_4,12H_2O$ is formed. The commercial nitrate is approximately $Th(NO_3)_4,4H_2O$. On heating the nitrate **thorium dioxide** (*thoria*) ThO_2 is formed as a white powder, m.p. >2800°, s. g. 9·69. (If 1 to 2 p.c. of sulphuric acid is present in the nitrate, this intumesces on heating and forms a finely divided ThO_2). ThO_2 forms cubic crystals isomorphous with CeO_2. The gas mantles usually contain a little magnesia and beryllium oxide to confer toughness. Thoria is also added to tungsten used to make some types of electric lamps. On the small scale thorium is purified by precipitating the iodate from a solution in mtric acid.

Metallic thorium, cubic, s. g. 11·3, m.p. 1845°, is difficult to obtain pure, as it combines with hydrogen, oxygen, nitrogen and carbon. It is prepared by heating $ThCl_4$ with sodium, or ThO_2 with $CaCl_2$ and calcium, or (less pure) by the electrolysis of a fused mixture of $ThCl_4$, NaCl and KCl (Marden and Rentschler, *Ind. Eng. Chem.*, 1927, **19**, 97; Driggs and Lilliendahl, *ibid.*, 1930, **22**, 1302). It is white, soft when pure, burns brightly in air just below a red heat, and is readily soluble in hydrochloric acid. A solid **hydride** ThH_4 of metallic appearance is formed, with emission of light, on heating thorium in hydrogen. It is not decomposed by water but dissolves in hydrochloric acid, especially on heating.

Thorium peroxide, perhaps $(HO)_3Th—O—OH$, which has no acidic properties, is quantitatively precipitated by hydrogen peroxide.

Thorium fluoride $ThF_4,4H_2O$ is only sparingly soluble in HF, like the rare earth fluorides (Ti and Zr fluorides are soluble). $K_2ThF_6,4H_2O$ is insoluble and amorphous. **Thorium chloride** $ThCl_4$, white rhombic crystals, m.p. 820°, subliming at 720°–750°, is formed by burning thorium in chlorine, heating ThO_2 and carbon in chlorine, or best by heating ThO_2 in $COCl_2$ or chlorine and S_2Cl_2 vapour. It is not hydrolysed by water and crystallises as $ThCl_4,8H_2O$. It shows little tendency to form complex salts, but $Cs_3[ThCl_7],12H_2O$ and $Cs_3[ThCl_6],11H_2O$ are known. The **bromide** $ThBr_4$ (by heating ThO_2 in HBr and S_2Cl_2 vapour) and **iodide** ThI_4 (by burning Th in I_2 vapour) are soluble.

A **basic carbonate** is precipitated by alkali carbonate and is readily soluble in excess but the solution becomes turbid on heating. The double carbonate $Na_6[Th(CO_3)_5],12H_2O$ is isomorphous with $Na_6[Ce(CO_3)_5],12H_2O$. Thorium salts are completely precipitated by $BaCO_3$ in the cold.

Thorium sulphide ThS_2, yellow-brown leaflets, is formed by passing H_2S over a heated mixture of $ThCl_4$ and NaCl, and washing with water. **Thorium sulphate** $Th(SO_4)_2$, made by dissolving ThO_2 in concentrated sulphuric acid, evaporating,

and heating to drive off the excess of acid, forms a number of hydrates, with 9, 8, 6, 4 and $2H_2O$. A solution of the anhydrous salt in four times its weight of ice water is metastable in respect of these. The hydrate with $9H_2O$ increases in solubility with rise of temperature, whilst that with $4H_2O$ decreases. The common hydrate is with $8H_2O$. **Acid sulphates** $H_2[Th(SO_4)_3]$ and $H_2[Th_2(SO_4)_5(H_2O)_2]$ and many **double sulphates,** *e.g.* $K_2[Th(SO_4)_3],4H_2O$, $Rb_2[Th(SO_4)_3],2H_2O$, $(NH_4)_2[Th(SO_4)_3],4H_2O$, $(NH_4)_4[Th(SO_4)_4],2H_2O$, $(NH_4)_6[Th(SO_4)_5],3H_2O$ and $(NH_4)_8[Th(SO_4)_6],2H_2O$ are known. There are also **double nitrates,** *e.g.* $(NH_4)_2Th(NO_3)_6$. The *radioactivity* of thorium is discussed on p. 202.

CHAPTER XIX

NITROGEN

The Fifth Group

Group V comprises (besides several radioelements, p. 204) the following elements :

Sub-group *a* or **even series** : vanadium, niobium (or columbium), tantalum, and protoactinium.

Sub-group *b* or **odd series** : nitrogen, phosphorus, arsenic, antimony, and bismuth.

Sub-group *a* (Even Series)

	V	Nb(Cb)	Ta	Pa
Atomic number	23	41	73	91
Electron configuration	2·8·11·2	2·8·18·12·1	2·8·18·32·11·2	2·8·18·32·18·11·2
Density	5·8	8·56	16·6	
Atomic volume	8·8	10·85	10·9	
Melting point	1710°	1950°	2850°	
Boiling point	3000°	3700°	> 4100°	

The elements of the even series are all less common metals of high m.p. and are **transitional elements** (p. 261).

Sub-group *b* (Odd Series)

	N	P	As	Sb	Bi
Atomic number	7	15	33	51	83
Electron configuration	2·5	2·8·5	2·8·18·5	2·8·18·18·5	2·8 18·32·18·5
Density of solid	1·0265	1·83*	5·73 †	6·71	9·80
Atomic volume	13·65	16·96	13·08	18·25	21·32
Melting point	−210°	44·1°	814·5°	630·5°	271°
Boiling point	−195·8°	287°	615° sublimes	1380°	1450°

The odd series contains both non-metals and metals. Nitrogen and phosphorus are definitely non-metals (although a " metallic " conducting form of phosphorus is known), antimony and bismuth definitely metals, whilst arsenic stands on the threshold between non-metals and metals and as such is sometimes called a *metalloid*. The elements all have low m.ps. and (except Sb and Bi) low b.ps. and form molecules in the vapour state composed of more than one atom : N_2, P_4, As_4, Sb_4 (?), Sb_2 (?), and Bi_2, the metals being peculiar in this respect, since most metals are monatomic (p. 5). All these elements exist in allotropic forms.

The predominating valencies in the group are 3 and (except for nitrogen) 5, although other valencies such as 4 (especially in the even series) are known ; nitrogen forms oxides, N_2O, NO, NO_2, in which it has apparently anomalous valencies ; although these are paralleled by oxides of vanadium, with nitrogen they usually result from peculiar linkages. The elements of the odd series all

* White P. † γ-arsenic.

form compounds with metals in which they show their normal valency (cf. p. 250): Mg_3N_2, Ca_3P_2, Na_3As, Zn_3Sb_2, Mg_3Bi_2.

The gradation of electrochemical character is well shown with the **gaseous hydrides** formed by all elements of the odd series. Ammonia NH_3, which is formed from its elements, is a fairly strong base, forming halide and oxysalts containing the ammonium ion NH_4^+; the other hydrides (except perhaps PH_3) are not formed directly; phosphine PH_3 is very weakly basic, forming only phosphonium halides PH_4X, which are all decomposed by water, and not oxysalts; arsine AsH_3 and stibine SbH_3 have no basic properties; the very unstable bismuth hydride BiH_3 (?) is soluble in alkalis and may be feebly acidic. Stable cations PR_4^+, AsR_4^+, SbR_4^+ are formed with alkyl radicals and form strongly basic hydroxides. The elements of the even series do not form hydrides. Elements of the odd series all form compounds with hydrocarbon radicals, including $Bi(CH_3)_3$, etc.; these are either not formed, or are doubtful, with elements of the even series.

The **chlorides** of the odd series are predominantly covalent; with nitrogen only NCl_3 is known and with arsenic and bismuth only $AsCl_3$ and $BiCl_3$, but AsF_5 and BiF_5 exist; all the other elements form RCl_3 and RCl_5, and in the even series chlorides corresponding with other valencies. Fluorides RF_3 are known with all the elements and RF_5 with P, As and Sb.* Nitrogen chloride hydrolyses in a peculiar way, forming hypochlorous acid (p. 438), the trihalides of phosphorus are completely and irreversibly hydrolysed by excess of water into HX and the corresponding oxyacids; arsenic chloride exists in equilibrium with excess of hydrochloric acid: $2AsCl_3 + 3H_2O \rightleftharpoons As_2O_3 + 6HCl$; antimony and bismuth trichlorides are only partly and reversibly hydrolysed to basic compounds, *e.g.* $BiCl_3 + H_2O \rightleftharpoons BiOCl + 2HCl$. The higher chlorides PCl_5 and $SbCl_5$ are dissociated by heat: $SbCl_5 \rightleftharpoons SbCl_3 + Cl_2$, etc., and on hydrolysis form oxyhalides, *e.g.* $POCl_3$, which by further action of water may lose all the halogen and form acids.

The stability of the halides MX_5 increases from V to Ta; only VF_5 is known, but tantalum is remarkable in forming a penta-iodide TaI_5. Double fluorides of varying formulae are known: xKF,VO_2F, xKF,$NbOF_3$ and xKF,TaF_5; from solutions containing excess of HF double fluorides containing VOF_3 and NbF_5 are formed. Isomorphous compounds are:

$2NH_4F,NbOF_3$ or $(NH_4)_2[Nb^{V}OF_5]$ $3KF,NbOF_3,HF$ or $K_3H[NbOF_7]$ $Zn[NbOF_5],6H_2O$
$2NH_4F,WO_2F_2$ or $(NH_4)_2[W^{VI}O_2F_4]$ $3KF,SnF_4,HF$ or $K_3H[Sn^{IV}F_6]$ $Zn[Ti^{IV}F_6],6H_2O$

All the elements form many **oxides**, including the typical acidic pentoxides R_2O_5. In the odd series only phosphorus, but in the even series all the elements, form pentoxides directly; the acidic character of these diminishes with increasing atomic weight. In the even series the acidity of the pentoxides decreases from V to Ta, V_2O_5 being quite strongly acidic, but the oxides Nb_2O_5 and Ta_2O_5 are more like the weakly acidic TiO_2 and ZrO_2. Vanadium, niobium and tantalum readily combine with oxygen and their compounds

* Iodides RI_3 and RI_5 (PI_5 is doubtful), also P_2I_4, are known, but ordinary nitrogen iodide is $NI_3{\cdot}NH_3$.

are difficult to reduce. The oxides of the odd series elements (except phosphorus) are easily reduced.

All the elements form trioxides R_2O_3 and most form dioxides RO_2 or R_2O_4. In the even series these are basic, but in the odd series the trioxides are acidic with N, P and As, amphoteric with Sb, and basic with Bi.

The **sulphides** are all formed from the elements except nitrogen sulphides. Those of nitrogen and phosphorus are peculiar (N_4S_4, N_2S_5; P_4S_3, P_2S_5) and readily hydrolysed; those of other odd series elements are typical (M_2S_3 and M_2S_5, except that bismuth forms only Bi_2S_3); those of the even series correspond with varying valencies. Many of the sulphides can form the electronegative constituent of complexes, *e.g.* Na_3AsS_4, $Na_2Sb_2S_4$ (or $NaSbS_2$), etc., *i.e.* are *thioanhydrides*.

Although vanadium compounds can be reduced to the stage V^{II} in solution, niobium stops at Nb^{III} and no salts below Nb^V have been isolated from solution; Ta^V is not reduced by nascent hydrogen. V_2O_5 can be reduced (with difficulty) to the metal by hydrogen at high temperature and pressure, Nb_2O_5 to Nb_2O_3, whilst Ta_2O_5 is not reduced.

The elements V, Nb and Ta form no nitrates or carbonates, and Nb and Ta no salts of weak acids, which are not well defined for vanadium.

Nitrogen

Scheele about 1770–72 proved that air is a mixture of two gases, *fire air* which supports combustion and respiration, and *foul air* which does not. Lavoisier (1775–6) gave a decisive proof of this, and called Scheele's foul air *azote* (Greek *a* no, *zoe* life); the name nitrogen (Greek *nitron*, nitre) was suggested by Chaptal in 1790. Daniel Rutherford (1772) and Priestley (1772) were independent discoverers of nitrogen, which Priestley called *phlogisticated air*.

Rayleigh and Ramsay in 1894 found that atmospheric nitrogen contains about 1 p.c. of an inert gas, as had been suspected by Cavendish in 1785. It was called argon (Greek *argon*, sluggish).

Air free from moisture and carbon dioxide contains roughly 4 vols. of nitrogen to 1 vol. of oxygen; more exact figures (Leduc, 1896) are:

	By weight.	By volume.
Nitrogen	75·5	78·06
Oxygen	23·2	21·00
Argon, etc.	1·3	0·94

Cavendish in 1783 found the composition of pure dry air sensibly constant: 20·833 vols. of oxygen and 79·167 vols. of nitrogen (including argon). Later analyses (Benedict, 1912; Paneth, *Nature*, 1937, **139**, 181; Carpenter, *J.A.C.S.*, 1937, **59**, 358) show that the volume percentages of oxygen and carbon dioxide in uncontaminated air are very constant:

	Volume p.c.	Weight p.c.
N_2	78·095	75·527
O_2	20·939	23·140
A	0·933	1·284
CO_2	0·031	0·047

Free nitrogen is found in volcanic gases and gas evolved from coal; the gas from some mineral springs may contain over 95 p.c. by vol. (Moureu, *J.C.S.*, 1923, **123**, 1905). Combined nitrogen occurs as ammonia, nitrites and nitrates, and in proteins (average 16 p.c. N) in organic matter, and radicals present in organic compounds (as well as some inorganic) are: $—NH_2$, $=NH$, $=NOH$, $—NO$, $—NO_2$, $—N=N—$ and $—N=N\rightarrow N$.

Atmospheric nitrogen, containing about 1 p.c. by vol. of inert gases, is obtained by removing oxygen from air (previously freed from carbon dioxide unless alkaline absorbents are used) by various methods (details in *College Course*, Chap. XXVIII):

(i) At room temperature by glowing phosphorus, moist iron filings, alkali polysulphide ("liver of sulphur"), alkaline pyrogallol (p. 656), hyposulphite ($Na_2S_2O_4$), chromous chloride ($CrCl_2$; some H_2 may be evolved), cuprous chloride in hydrochloric acid or ammonia solution, or copper turnings in presence of ammonia solution, which may be saturated with ammonium carbonate or chloride. The ammoniacal solution can be circulated over copper turnings in a tower through which air is passed (Berthelot, 1870; Van Brunt, *J.A.C.S.*, 1914, **30**, 1448, Badger, *Ind. Eng. Chem.*, 1919, **11**, 1052).

(ii) At higher temperature by passing air or a mixture of air and ammonia gas over red-hot copper turnings. In the second case (Vernon Harcourt and S. Lupton, *Chem. News*, 1876, **33**, 90; Hutton and Petavel, *J.S.C.I.*, 1904, **23**, 87) the ammonia hydrogen combines with the atmospheric oxygen and the mixture of Cu and CuO formed prevents the passage of any free oxygen or ammonia: $4NH_3 + 3O_2 = 2N_2 + 6H_2O$, and $2NH_3 + 3CuO = N_2 + 3H_2O + 3Cu$. The gas is a mixture of pure and atmospheric nitrogen.

On the large scale nitrogen is made by the *fractionation of liquid air* (p. 653). Besides its use in ammonia synthesis (p. 550) it is used in some types of gas-filled electric lamps (p. 890). The b.ps. of the constituents of air are: Ne 27°, N_2 77°, A 87°, O_2 90° abs., so that the argon tends to accumulate in the oxygen fraction. The commercial nitrogen contains a little oxygen which is removed by passing through a long tube of copper turnings at a bright red heat.

The volumetric composition of air.—The oxygen in a measured volume of air may be removed by absorbents and the contraction measured. The most *accurate* method is to explode a measured volume of air with excess of hydrogen over mercury. The hydrogen unites with the oxygen to form water which condenses to a liquid of negligible volume, hence the volume of oxygen is *one-third* of the measured contraction. A convenient apparatus is the **Hempel burette and absorption pipette** (Fig. 234).

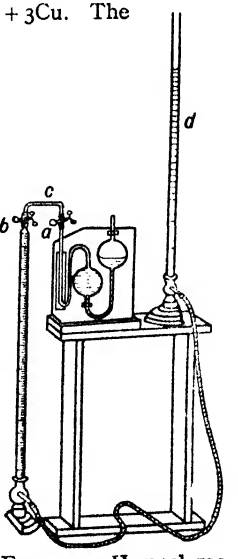


FIG. 234.—Hempel gas burette and pipette.

The burette and levelling tube are mounted on wooden stands weighted with lead and cut so that the two tubes may be brought close together. Connection

with the pipette is made by glass capillary tube and rubber *pressure* tubing and the burette is closed with a spring clip.* The burette and capillary tube are filled with water and the sample of gas from the pipette is drawn into the burette and measured, water from the pipette being passed over to fill the capillary tube. The pipette is then filled with a suitable absorbent, re-connected with the burette and the gas passed into the pipette. After shaking, the gas is passed back into the burette and measured. If necessary the burette and pipette containing the gas sample may be filled with mercury. Suitable absorbents are concentrated caustic potash solution for carbon dioxide, alkaline pyrogallol for oxygen, ammoniacal cuprous chloride for carbon monoxide and acetylene, ferrous sulphate solution for nitric oxide, bromine water for ethylene.

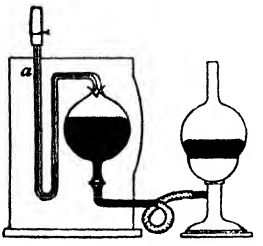


FIG. 235.—Explosion pipette.

If gases are to be exploded, an **explosion pipette** (Fig. 235) fitted with platinum sparking wires is used, the gas being confined over mercury. The gas and oxygen are measured separately in the burette and passed into the explosion pipette, in which the mixture is sparked, the tap being closed and the pressure tubing on the pipette being closed by a strong screw clip and a piece of glass rod.

The gravimetric composition of air.—The determination of the composition of air *by weight* is carried out by the method of Dumas and Boussingault (1841), in which air is passed over a weighed column of red-hot copper, the increase in weight of which gives the oxygen, and the nitrogen is collected and weighed in a vacuous globe.

A long tube of hard glass packed with bright copper turnings and fitted with a stopcock at each end is connected at one end with a large weighed vacuous globe closed by a stopcock and at the other with a bulb of potash solution and two U-tubes, one containing solid caustic potash and the other calcium chloride, which remove carbon dioxide and moisture from the air (Fig. 236).

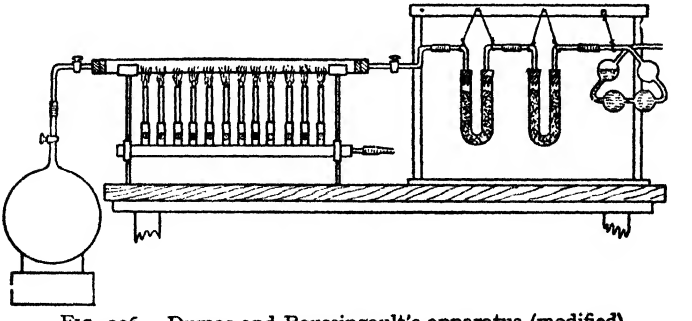


FIG. 236.—Dumas and Boussingault's apparatus (modified).

The tube containing the copper is evacuated and weighed, put in the furnace, and heated to bright redness. The stopcocks are slightly opened and the dry

* Burettes with glass taps are more expensive.

purified air allowed to pass *slowly* over the heated copper, the oxygen being absorbed to form copper oxide and the nitrogen passing on into the globe. When the globe is full of nitrogen the stopcocks are closed and the apparatus allowed to cool. The globe is weighed and the weight of nitrogen found. The tube containing the copper and copper oxide is now weighed. The *nitrogen in this tube* is removed by a pump and the vacuous tube again weighed in order to find the weight of this nitrogen, which is added to that in the globe. The increase in weight of the *vacuous* tube gives the weight of oxygen.

The nitrogen as weighed contains the argon and other inert gases. These can be determined by repeatedly passing the nitrogen over red-hot magnesium, when only the inert gases remain, the nitrogen forming magnesium nitride. Dumas and Boussingault found that 100 parts by weight of air contain 23·00 parts of oxygen and 77·00 of " nitrogen " (nitrogen + argon).

Air is a mixture not a chemical compound.—That air is a mixture and not a compound of oxygen and nitrogen follows from the facts given below:

(i) Although the composition (when free from water and carbon dioxide) is *very nearly*, it is not quite constant. The atomic ratio is not simple but corresponds with $N_{79}O_{21}$.

(ii) The constituents may be partly separated by diffusion of air through a porous pipeclay tube into a vacuum (atmolysis), when the nitrogen passes through more rapidly than the oxygen.

(iii) The constituents may be separated by fractional distillation of liquid air.

(iv) When air is shaken with water, the dissolved part is richer in oxygen than the undissolved part (p. 56).

(v) When oxygen and nitrogen are mixed there is no evolution or absorption of heat, and the properties (specific heat, refractive index, etc.) of the mixture are intermediate between those of the constituents.

(vi) The density of air corresponds with a mixture $4N_2 + O_2$, not a compound N_4O.

Preparation of nitrogen from its compounds.—*Pure nitrogen* is made from its compounds. In small quantities, it is evolved by heating sodium or barium azide in a vacuum: $Ba(N_3)_2 = Ba + 3N_2$. Usually it is prepared by the removal of hydrogen from ammonia: $2NH_3 = 3H + N_2$, by the action of chlorine, bromine, hypochlorite or hypobromite in the cold, by copper oxide, nitric oxide, nitrous acid (in ammonium nitrite) or chromic acid (in ammonium dichromate) at higher temperature.

(1) Chlorine gas passed slowly into concentrated (s. g. 0·880) ammonia reacts with feeble flashes of light and nitrogen is evolved (Fourcroy, 1789): $2NH_3 + 3Cl_2 = N_2 + 6HCl$.

The ammonia must be in excess (when fumes of ammonium chloride are formed: $HCl + NH_3 = NH_4Cl$), otherwise dangerously explosive liquid nitrogen trichloride (p. 555) is formed. This nitrogen contains a little oxygen. Bromine dropped into ammonia solution reacts similarly (in this case no explosive nitrogen bromide is formed).

(2) Hypochlorite and hypobromite solutions evolve nitrogen with ammonia: $2NH_3 + 3OCl' = N_2 + 3Cl' + 3H_2O$. (With excess of hypochlorite nitrogen trichloride is formed.)

EXPT. 1.—To 100 c.c. of concentrated ammonia in a flask add gradually a thin paste of 40 g. of bleaching powder, with a little milk of lime, through a thistle funnel. Nitrogen is evolved with frothing on warming :

$$3Ca(OCl)_2 + 4NH_3 = 3CaCl_2 + 6H_2O + 2N_2.$$

EXPT. 2.—Add 6 c.c. of bromine to a solution of 10 g. of caustic soda in 100 c.c. of water in a flask cooled by running water. Ammonia solution is dropped in : $3NaOBr + 2NH_3 = 3NaBr + 3H_2O + N_2$. Nitrogen is also evolved by the action of alkaline hypobromite solution on urea :

$$CON_2H_4 + 3NaOBr = CO_2 + N_2 + 2H_2O + 3NaBr.$$

The gas contains a trace of nitrous oxide N_2O which is removed by passing over red-hot copper (Rayleigh, *Proc. Roy. Soc.*, 1898, **64**, 95).

(3) A convenient method is the decomposition by heat of a solution of ammonium nitrite (Corenwinder, 1849) : $NH_4NO_2 = N_2 + 2H_2O$. A solution of sodium nitrite and ammonium chloride is heated gently and nitrogen is evolved : $NaNO_2 + NH_4Cl = NaCl + N_2 + 2H_2O$.

The gas contains a little nitric oxide ; if a solution of 1 pt. of $NaNO_2$, 1–2 pts. of $(NH_4)_2SO_4$ and 1 pt. of $K_2Cr_2O_7$ is heated and the gas washed with dilute sulphuric acid the nitrogen is free from nitric oxide.

The decomposition of ammonium nitrite occurs quickly only in faintly acid solution and seems to involve free nitrous acid (Millon, 1847 ; Arndt, *Z. phys. Chem.*, 1901, **39**, 64 ; 1903, **45**, 571) : $HNO_2 + NH_3 = N_2 + 2H_2O$.

EXPT. 3.—Dissolve 30 g. of sodium nitrite in the smallest amount of cold water and add a cold saturated solution of 22 g. of ammonium chloride. Filter. Make 5 c.c. of the solution mixed with 20 c.c. of water faintly alkaline with a drop of ammonia, and another 5 c.c. + 20 c.c. of water faintly acid with a drop of dilute sulphuric acid. Heat the solutions in beakers over two small equal flames and observe the results. Dilute the main quantity of the ammonium nitrite solution, heat in a flask, and collect the gas over water.

(4) A mixture of nitric oxide and ammonia when passed over red-hot copper gives pure nitrogen (Baxter and Hickey, 1905) : $6NO + 4NH_3 = 5N_2 + 6H_2O$.

(5) Solid ammonium dichromate decomposes violently with incandescence on heating, a voluminous green powder of chromic oxide remaining :

$$(NH_4)_2Cr_2O_7 = Cr_2O_3 + N_2 + 4H_2O.$$

The gas contains traces of ammonia and oxides of nitrogen.

Nitrogen is a colourless, odourless, tasteless gas, does not support combustion or respiration (although it is not poisonous), is sparingly soluble in water, has no action on litmus and does not turn lime water milky. Its physical properties are :

Critical temperature	−147·13°	Melting point	−210·5°/86 mm.
Critical pressure	33·49 atm.	S. g. of liquid at b.p.	0·8042
Boiling point	−195·81°	Normal density of gas	1·2505 g./lit.

Liquid nitrogen is colourless ; on rapid evaporation it forms the ice-like solid (cf. oxygen, p. 655). A second form of the solid is formed at −237·5°.

There are two isotopes, ^{14}N and ^{15}N (Naudé, 1930) : enrichment in ^{15}N to 2·4 p.c. is achieved by an exchange reaction between ammonia gas and ammonium sulphate solution (Urey, etc., *J.A.C.S.*, 1937, **59**, 1407).

The electronic formulae of the nitrogen and carbon monoxide molecules, and of the cyanide ion, are very similar :

$$:N:::N: \qquad \overset{\times}{\underset{\times}{C}}::O: \qquad [\overset{\times}{\underset{\times}{C}}::N:]'$$
$$N\equiv N \qquad C\leqq O \qquad C\leqq N'$$

In the last case, an extra electron must be introduced to complete the octet on the nitrogen atom, thus producing a univalent anion.

Nitrogen is inert, since the heat of dissociation of the molecule is large, 170 k. cal. per mol : it combines directly but slowly with hydrogen and with oxygen on sparking, and with some metals to form nitrides.

Nitrides.—Some metals combine directly with nitrogen. *Lithium* combines slowly at room temperature, more rapidly on heating, to form Li_3N. *Magnesium*, *calcium*, *strontium* and *barium* at a red heat form nitrides M_3N_2. *Boron* and *aluminium* form BN and AlN at a bright red heat ; *silicon* forms Si_3N_4 only at a white heat. Nitrides of many metals are formed by heating the finely divided metals, or the oxides or salts, in ammonia gas.

Some special methods for the preparation of nitrides are :

(i) Heating the metal amides : $3Ba(NH_2)_2 = Ba_3N_2 + 4NH_3$. The alkali metal amides do not form nitrides in this way.

(ii) By striking an electric arc between a platinum cathode and an alkali metal anode under liquid nitrogen, explosive nitrides of alkali metals Na_3N, K_3N, and Rb_3N are said to be formed.

(iii) By reactions between potassamide and metal salts dissolved in anhydrous liquid ammonia, some metal nitrides are precipitated :

$$3HgI_2 + 6KNH_2 = Hg_3N_2 + 6KI + 4NH_3$$
$$3TlNO_3 + 3KNH_2 = Tl_3N + 3KNO_3 + 2NH_3.$$

Lithium nitride and magnesium nitride are decomposed by cold water, the alkaline-earth nitrides by hot water, boron and aluminium nitrides by heating in steam. In all cases the oxide or hydroxide and ammonia are formed ; *e.g.* : $Mg_3N_2 + 3H_2O = 3MgO + 2NH_3$.

Active nitrogen.—Morren in 1865 noticed a yellow after-glow in nitrogen subjected to an electric discharge. R. J. Strutt (now Lord Rayleigh) in 1911 showed that this was due to a modification of nitrogen, more active than ordinary nitrogen, and called *active nitrogen*. It is formed by subjecting a current of nitrogen drawn through a tube *A* at less than 2 mm. pressure, to a high tension electric discharge with a condenser in circuit (Fig. 237). The gas beyond the discharge glows with a yellow light. It is also obtained by an electrodeless or an arc discharge in nitrogen at

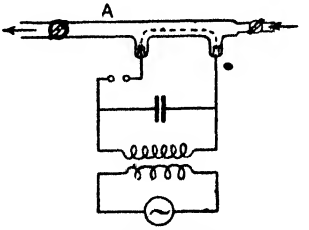


FIG. 237.—Preparation of active nitrogen.

low pressure. If electrodes are used they should be of aluminium or degassed iron, not platinum.

The glow is not produced in very pure nitrogen, made by heating barium azide, and traces of impurities in the gas are necessary. Traces of oxygen, mercury vapour, etc., are active; 0·001 p.c. of oxygen is sufficient and more than 0·005 p.c. is injurious: a glow obtained with air is said by Rayleigh to be due to a reaction between ozone and nitric oxide.

The spectrum of the glow is very complicated, and indicates that both nitrogen atoms amd nitrogen molecules in excited states are present in the gas. The glow is not due to ionised nitrogen, since it persists when charged particles are removed from the gas.

The chemical properties of active nitrogen include the following. It does not react with molecular hydrogen or oxygen, but forms ammonia with atomic hydrogen. It combines with sulphur, phosphorus, sodium, calcium, aluminium, mercury and some other metals, forming nitrides; with acetylene it forms hydrocyanic acid, and with nitric oxide it forms nitrogen and oxygen (which reacts with excess of NO to form NO_2). It decomposes hydrogen iodide and, less easily, hydrogen bromide, but not hydrogen chloride.

There has been much controversy on the nature of active nitrogen, and the problem is not yet solved. Lord Rayleigh supposed that it is atomic nitrogen, and many lines of evidence show that nitrogen atoms are present in the gas. These probably account for its chemical activity. Saha and Sur (1924) suggested that active nitrogen consists of metastable nitrogen molecules, *i.e.* excited molecules with a relatively long life. It seems probable that both normal and excited atoms and molecules are present. The glow and chemical activity seem to be inseparable. Since the rate of disappearance of active nitrogen is bimolecular with respect to atomic nitrogen, and a third body is assumed to be necessary to remove the energy of combination of the atoms, the glow is supposed to be the result of a termolecular reaction between two nitrogen atoms, one probably excited, and a nitrogen molecule: $N + N' + N_2 = 2N_2$. This would agree with the long life of the glow-emitting reaction and with the negative temperature coefficient of the decay of the glow (cf. the negative temperature coefficient of the reaction $2NO + O_2 = 2NO_2$). The effect of traces of impurities is attributed to their adsorption on the walls of the vessel, thus preventing recombination of nitrogen atoms by collision with the surface and forcing the glow reaction into the body of the gas. In a bulb coated with metaphosphoric acid the glow persists for some hours.

Compounds of Nitrogen and Hydrogen

Nitrogen and hydrogen form the basic substances **ammonia** NH_3 and **hydrazine** N_2H_4, and **hydrazoic acid** HN_3. The basic **hydroxylamine** NH_2OH, as a derivative of ammonia, is usually included in this group. Compounds of hydrazoic acid with ammonia and hydrazine have the empirical formulae N_4H_4 and N_5H_5, respectively.

AMMONIA

Ammonium chloride NH_4Cl, *sal ammoniac*, was obtained in the Middle Ages from Central Asia or made in Egypt from the soot from burning camels' dung. Gaseous ammonia was obtained by Priestley in 1774 by collecting over mercury; he called it *alkaline air* and found that on sparking it gave twice its volume of combustible gas. Berthollet (1785) showed that nitrogen and hydrogen are formed in this decomposition: $2NH_3 = N_2 + 3H_2$, and the result was confirmed and the formula NH_3 established by Austin (1788), Davy (1800), and Henry (1809).

Traces of ammonia occur in the atmosphere, and bottles containing hydrochloric acid become coated with ammonium chloride. Ammonium chloride and sulphate occur in volcanic districts, and ammonia accompanies boric acid in the *soffioni* of Tuscany. Ammonium salts occur in plants and animals (*e.g.* in blood and in urine), in rock salt, in the soil, and in natural waters (as nitrite and nitrate), and ammonia is formed in the putrefaction of nitrogenous organic matter.

Ammonia is formed from its elements when these are sparked together: $N_2 + 3H_2 \rightleftharpoons 2NH_3$ (Regnault, 1840). Deville (1864) showed that sparks both form and decompose ammonia, and a state of equilibrium is set up with about 6 p.c. of NH_3. If the mixture $N_2 + 3H_2$ and pure ammonia are exposed to prolonged sparking, contraction ensues in the first case and expansion in the second, until the volumes and compositions are the same. Small quantities of ammonia are formed from the elements by a silent discharge (Donkin, 1873).

EXPT. 4.—Spark a mixture of nitrogen and hydrogen over mercury in a eudiometer containing a little concentrated sulphuric acid. Observe the gradual contraction, owing to formation of ammonia.

Ammonia gas is evolved on warming the concentrated solution (s. g. 0·880) or on heating ammonium chloride with dry slaked lime:

$$2NH_4Cl + Ca(OH)_2 = CaCl_2 + 2NH_3 + 2H_2O.$$

EXPT. 5.—Mix 50 g. of powdered ammonium chloride with 150 g. of powdered slaked lime in a mortar, transfer to a 250 c.c. flask, and fill up with small lumps of quicklime. Fit a cork and delivery tube, leading to a drying tower filled with lumps of quicklime, heat on wire gauze, and collect the gas by upward displacement (Fig. 238). Ammonia is not easily dried. Concentrated sulphuric acid reacts violently, forming ammonium sulphate, and calcium chloride absorbs it, forming a compound, $CaCl_2,8NH_3$.

Unless very pure and almost completely dry it reacts with pure phosphorus pentoxide (Baker, *J.C.S.*, 1894, **65**, 611; Smits, *Z. phys. Chem.*,

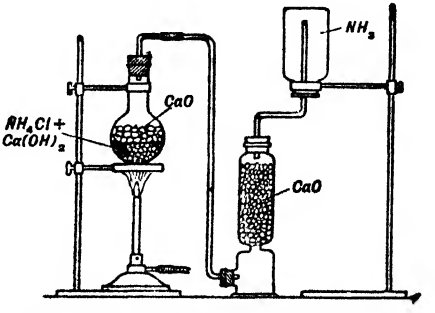


FIG. 238.—Preparation of ammonia gas.

1935, **28B**, 31). It is best to pass the gas slowly over broken freshly fused caustic potash, liquefy it in a bulb containing sodium (cooled only in the lower part) and distil the blue liquid (p. 317) formed (Hart and Partington, *J.C.S.*, 1943, 104).

Ammonia is evolved on heating ammonium sulphate : $(NH_4)_2SO_4 = NH_4HSO_4 + NH_3$, ammonium phosphate : $(NH_4)_2HPO_4 = 2NH_3 + HPO_3 + H_2O$, and microcosmic salt : $NH_4NaHPO_4 = NH_3 + NaPO_3 + H_2O$; by heating ammonium salts with alkalis (*e.g.* 170 g. of ammonium sulphate and 250 c.c. of 50 p.c. NaOH solution) : $(NH_4)_2SO_4 + 2NaOH = Na_2SO_4 + 2NH_3 + 2H_2O$, and ammonium chloride with lead oxide : $2NH_4Cl + PbO = 2NH_3 + PbCl_2 + H_2O$.

Ammonia is formed by the reduction of oxygen compounds of nitrogen (except nitrous oxide), *e.g.* on passing a mixture of hydrogen and nitric oxide or a higher oxide of nitrogen or nitric acid vapour over heated platinum : $2NO + 5H_2 = 2NH_3 + 2H_2O$.

Dilute nitric acid is reduced by nascent hydrogen from zinc and dilute sulphuric acid : $HNO_3 + 8H = NH_3 + 3H_2O$; sodium nitrate, or more readily nitrite, by zinc or aluminium and hot alkali hydroxide solution, but most easily in alkaline solution by powdered Devarda's alloy (45 pts. of aluminium, 50 of copper, and 5 of zinc). This method is used for the estimation of nitrates or nitrites.

Ammonia is a colourless gas with a strong pungent smell. It is lighter than air, normal density 0·771 g./lit., easily liquefied by cold or pressure, forming a colourless liquid, density 0·6386 at 0°, b.p. −33·4°, freezing to an ice-like solid, m.p. −77·7° ; critical temperature 132·5°, critical pressure 111·2·30 atm. The liquid is obtained by cooling with a mixture of ice and crystalline calcium chloride, or on a large scale by compressing the gas into steel coils cooled with water, and is sold in steel cylinders for use in refrigeration apparatus. The latent heat of evaporation at the b.p. is 327 g. cal. per g.

The solubility in water by volume (1148 vols. in 1 vol. H_2O at 0° and 739 at 20°) is greater for ammonia than for any other gas. The solution is alkaline : $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH'$. This can be shown with the " fountain experiment " (*College Course*, p. 158) using water coloured with red litmus, which turns blue. Ammonia solution is made by passing the gas into distilled water kept cool ; much heat is evolved ($NH_3 + Aq. = NH_3Aq. + 8{\cdot}4$ k. cal.), and the liquid expands. The s. gs. ($D_{15{\cdot}5}^{15{\cdot}5}$) at 15·5° are :

S. g.	$\%NH_3$	S. g.	$\%NH_3$
0·875	36·90	0·950	12·74
0·880	35·20	0·960	9·95
0·890	31·85	0·970	7·27
0·900	28·50	0·980	4·73
0·910	25·15	0·990	2·31
0·920	21·85	0·992	1·84
0·930	18·69	0·996	0·91
0·940	15·65	0·998	0·45

By strong cooling two crystalline hydrates are formed (Rupert, *J.A.C.S.*, 1909, **31**, 866 ; Elliott, *J. Phys. Chem.*, 1924, **28**, 887), $NH_3.H_2O$, m.p. −79·0°,

and $2NH_3,H_2O$, m.p. $-78{\cdot}9°$. With concentrated hydrogen peroxide the compounds NH_3,H_2O_2 and $2NH_3,H_2O_2$ are formed on cooling (Maas and Hatcher, *J.A.C.S.*, 1922, **44**, 2472).

The solubility of ammonia in water obeys Henry's law only up to normal concentration, or above 100°, when it is small; all the gas is evolved on boiling. 1 lit. of alcohol dissolves 130 g. of ammonia at 0°.

The solution of ammonia in water has been supposed to contain ammonium hydroxide NH_4OH, with free ammonia: $NH_4OH \rightleftharpoons NH_4^{\cdot} + OH'$. The weakness of NH_4OH (also of amines) has been explained as due to removal of OH' ions by the lone pair of electrons on the oxygen forming a covalent link with the hydrogen attached to nitrogen (Moore and Winmill, *J.C.S.*, 1912, **101**, 1635): $[R_3NH]^+ + OH^- = R_3NH{\leftarrow}OH$ (R = Me, Et, etc.). The quaternary ammonium hydroxides, with no hydrogen attached to nitrogen, cannot form such covalent compounds and are powerful bases: $[R_4N]^+ + OH^-$. Ammonium hydroxide is a weak base; the ionisation constant $[NH_4^{\cdot}][OH']/[NH_3 \text{ total}]$ at 18° is $1{\cdot}8 \times 10^{-5}$.

Ammonia gas is decomposed by heated alkali metals and barium, when metal **amides** (*e.g.* sodamide) containing the $-NH_2$ group are formed and hydrogen is evolved: $2NH_3 + 2Na = 2NaNH_2 + H_2$.

EXPT. 6.—Pass dry ammonia over potassium heated in a hard glass bulb tube. The metal boils, emitting a green vapour, and reaction begins. The hydrogen may be kindled, and a brown mass of impure potassamide is left in the tube.

The alkali metal amides are violently decomposed by water, with evolution of ammonia: $NaNH_2 + HOH = NaOH + NH_3$.

Ammonia is fairly stable, not easily decomposed by heat especially if diluted with an indifferent gas, but more easily on the surface of an iron catalyst. It is completely decomposed by ultra-violet light and radium emanation. Ammonia gas is not combustible in air and does not support combustion, but the flame of a taper is surrounded by a large greenish-yellow flame, due to decomposition of ammonia: $2NH_3 = N_2 + 3H_2$. The gas burns in oxygen with a greenish-yellow flame, and a mixture of ammonia and oxygen explodes when kindled: $4NH_3 + 3O_2 = 6H_2O + 2N_2$.

EXPT. 7.—Pass a current of ammonia gas through a tube surrounded by a wider tube through which oxygen gas is passing (Fig. 239). If a taper is held over the tubes, the ammonia burns with a large three-coned yellowish flame.

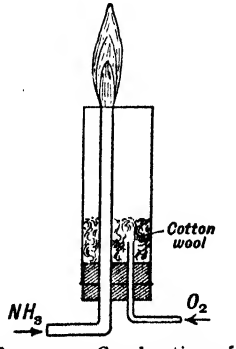


FIG. 239.—Combustion of ammonia in oxygen.

In contact with heated platinum, a mixture of ammonia gas and air or oxygen is catalytically oxidised to nitric oxide: $4NH_3 + 5O_2 = 4NO + 6H_2O$.

EXPT. 8.—Pass oxygen through 50 c.c. of concentrated ammonia warmed in a 200 c.c. conical flask and suspend a red-hot spiral of platinum wire in the flask.

The mixture of ammonia and oxygen explodes feebly: $4NH_3 + 3O_2 = 6H_2O + 2N_2$. The wire cools but after a short time it heats up and there is finally another explosion when the mixture is renewed. During oxidation without explosion, red oxides of nitrogen and white fumes of ammonium nitrate are formed: $4NH_3 + 5O_2 = 4NO + 6H_2O$; $2NO + O_2 = 2NO_2$; $4NO_2 + O_2 + 2H_2O + 4NH_3 = 4NH_4NO_3$. A jet of oxygen will burn under the surface of the ammonia solution.

Schlumberger and Piotrowski (1914) found that mixtures with air containing 16·5 to 26·8 p.c. of ammonia can be exploded by an electric spark in a spherical glass vessel. Berl and Bausch (1929) found that only the mixture with 21·9 p.c. of ammonia ($4NH_3 + 3O_2$) can be exploded by a heated silver wire in a metal container at atmospheric pressure: at higher pressures mixtures on both sides of this composition are explosive.

Mixtures of ammonia with electrolytic gas ($2H_2 + O_2$) are explosive when the volume ratio of this to ammonia is slightly greater than 1, when 79 p.c. of the ammonia is decomposed. When the ratio exceeds 3 the ammonia is completely decomposed, the gaseous product containing only nitrogen, hydrogen and steam. Explosion of ammonia with deficiency of oxygen, so that the steam remains gaseous, causes complete decomposition, oxides of nitrogen being formed only if the ratio of NH_3 to O_2 is less than 1 to 1·6. With the ratio 1 to 1·22 the oxidation of nitrogen is a maximum (16 p.c.). When oxides of nitrogen are formed, the colour of the flame changes from yellow to green, violet and white, and the nitrogen oxidised is greater than with a corresponding mixture of nitrogen, hydrogen and oxygen (Partington and Prince, *J.C.S.*, 1924, **125**, 2018).

When ammonia is exploded with a mixture of carbon monoxide and oxygen ($2CO + O_2$) a practically constant fraction (95·3 p.c.) is decomposed with all ignitible mixtures (Beeson and Partington, *J.C.S.*, 1925, **127**, 1146).

Ammonia reduces many heated oxides of metals (*e.g.* CuO, PbO): $3PbO + 2NH_3 = 3Pb + N_2 + 3H_2O$. Ammonia gas may be detected by (1) its smell, (2) the blueing of moist red litmus paper, (3) the white fumes of ammonium chloride formed around a glass rod dipped in concentrated hydrochloric acid, (4) blackening a piece of paper dipped in mercurous nitrate solution, (5) the brown precipitate with Nessler reagent (p. 400).

Liquid ammonia is a good *solvent* for many salts (chlorides, bromides, iodides, cyanides, thiocyanates and nitrates, but not fluorides, sulphates, phosphates, carbonates, etc.) and other substances (I_2, S, P, alkali metals, organic amides, nitro-compounds, alkyl ammonium bases and their salts, etc.) and many interesting reactions occur in it (Franklin, *The Nitrogen Series of Compounds*, 1935; Findlay, *J.C.S.*, 1938, 583).

Some heavy metal amides: $KNH_2 + AgNO_3 = KNO_3 + AgNH_2$, and orange-red lead imide: $2KNH_2 + PbI_2 = 2KI + NH_3 + PbNH$, are precipitated by potassamide in liquid ammonia. These compounds are usually explosive. Reactions in liquid ammonia parallel those in water if the ionisations are represented as $2H_2O \rightleftharpoons H_3O^+ + OH^-$ and $2NH_3 \rightleftharpoons NH_4^+ + NH_2^-$ (see p. 162). Acid amides behave as *ammono-acids*: $R{\cdot}CO{\cdot}NH_2 \rightleftharpoons R{\cdot}CO{\cdot}NH^- + H^+ \rightleftharpoons R{\cdot}CO{\cdot}N^{--} + 2H^+$, and metal amides as *ammono-bases*: $KNH_2 \rightleftharpoons K^+ + NH_2^-$, "neutralisation" involving combination of NH_4^+ and NH_2^-. "Ammonolysis" corresponds with hydrolysis: $HgCl_2 + (NH_2^- + NH_4^+) = HgNH_2Cl + NH_4Cl$.

Ammonia gas is absorbed by many salts to form *ammines*, analogous to hydrates:

$CaCl_2$ with 8 and 4 NH_3	LiCl with 4, 3 and $2NH_3$
$CaBr_2$ with 8, 6, 2 and $1NH_3$	LiBr with 5, 4, 3, 2 and $1NH_3$
$FeCl_2$ with 8, 6, 2 and $1NH_3$	LiI with 4, 3, 2 and $1NH_3$
$NiCl_2$ with 6 and $2NH_3$	$CuSO_4$ with 5, 4, 2 and $1NH_3$
$MnCl_2$ with 6, 2 and $1NH_3$	AgCl with 3, 2, $1\frac{1}{2}$, 1 and $\frac{1}{2}NH_3$

Analogous compounds are formed with heavy ammonia ND_3 (Hart and Partington, *J.C.S.*, 1943, 104). If the compound $AgCl,3NH_3$ is sealed up in one limb of a bent tube (Fig 16) and warmed, liquid ammonia collects in the other, cooled, limb. Ammonium nitrate absorbs a third of its weight of ammonia at 12° to form *Divers' liquid*, and dry NH_4CNS absorbs nearly half its weight of ammonia at 0°. Both liquids evolve ammonia on warming. A solid compound $NH_4NO_3,3NH_3$ separates at $-40°$.

The *formula of ammonia* may be found in several ways.

(i) The gas when sparked for some time gives almost double the volume of gas (a little ammonia remains, see p. 545), and by sparking this with excess of oxygen, and measuring the contraction (two-thirds of which gives the volume of hydrogen: $2H_2 + O_2 = 2H_2O$ liq.) and the volume of residual nitrogen after absorbing the excess of oxygen by alkaline pyrogallol, it is found that 2 vols. of gas give 1 vol. of N_2 and 3 vols. of H_2. Hence $2N_xH_y$ (2 vols.) $= N_2 + 3H_2$ (total 4 vols.). Hence $x = 1$ and $y = 3$ and the formula is NH_3. This is *confirmed* by the density of ammonia, which gives the molecular weight 17.

(ii) Electrolysis of a mixture of 10 vols. of saturated sodium chloride solution and 1 vol. of concentrated ammonia (s. g. 0·880) gives 1 vol. of nitrogen at the anode and 3 vols. of hydrogen at the cathode (Hofmann, 1869; Szarvasy, *J.C.S.*, 1900, **77**, 603).

(iii) In Hofmann's experiment (1865) a long tube marked into three equal volumes is filled with chlorine and concentrated ammonia cautiously let in through the tap (Fig. 240), the tube being cooled. The first portions give yellowish-green flames and solid ammonium chloride deposits: $3Cl_2 + 8NH_3 = 6NH_4Cl + N_2$. Dilute sulphuric acid is added to fix the excess of ammonia, the tube above the tap is filled with water and a tube filled with and dipping into boiled water is fitted on by a cork. On opening the tap water enters and 1 vol. of nitrogen remains in the tube. The 3 vols. of chlorine have combined with 3 vols. of hydrogen to form hydrochloric acid, hence the formula of ammonia is $(NH_3)_x$. The density shows that $x = 1$.

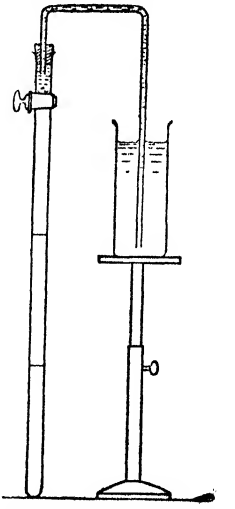


FIG. 240.—Hofmann's experiment on the composition of ammonia.

(iv) The gravimetric composition is found by passing a known weight of ammonia gas through a tube

containing red-hot copper oxide followed by copper turnings heated to bright redness to decompose any nitric oxide :

$$2NH_3 + 3CuO = 3Cu + N_2 + 3H_2O$$
$$2NH_3 + 5CuO = 5Cu + 2NO + 3H_2O.$$

The water vapour is absorbed in a weighed calcium chloride tube and the nitrogen collected and weighed in a vacuous globe as described on p. 540. The weight ratio found is N : H = 14 : 3, hence the formula is $(NH_3)_x$; the density gives $x = 1$.

The molecules NH_3, PH_3 and AsH_3 (probably SbH_3) in the gases are flat tetrahedra, the heavy atom probably vibrating through the plane of the hydrogens (Mills, *J.C.S.*, 1943, 194). The crystals are cubic (Mark and Pohland, 1925). The three valencies of doubly linked nitrogen —N= are not co-planar (Mills and Bain, *J.C.S.*, 1910, **97**, 1866 ; 1914, **105**, 64).

Manufacture of ammonia.—Ammonia and ammonium salts are made from *gas-liquor*, a by-product of coal gas or coke manufacture (p. 456), but this source is now unimportant as compared with the synthesis from atmospheric nitrogen.

Bituminous coal contains about 1 p.c. of nitrogen, part of which is recovered in carbonisation, mainly as ammonia in the form of *ammoniacal liquor*. The average yield in gas-works and coke-ovens is 20–25 lb. of ammonium sulphate per ton of coal, representing less than 20 p.c. of the nitrogen content.

The ammoniacal liquor is heated with steam in an ammonia still (Fig. 241) to drive out the free ammonia and milk of lime added to decompose the ammonium salts. The ammonia gas is bubbled into 60 p.c. sulphuric acid in a lead-lined tank, when crystals of ammonium sulphate separate.

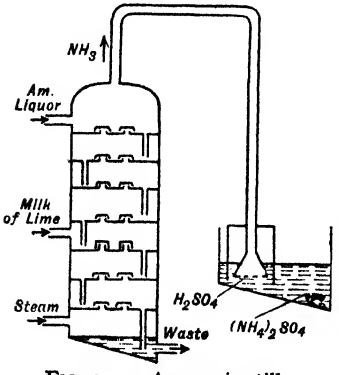


FIG. 241.—Ammonia still.

Synthetic ammonia is now largely made. A mixture of pure hydrogen and nitrogen in the ratio 3 vols. to 1 under pressure in presence of an iron catalyst forms ammonia : $N_2 + 3H_2 \rightleftharpoons 2NH_3$. Heat is evolved and the equilibrium shifts to the left at higher temperatures. The volume decreases and hence the equilibrium shifts to the right at higher pressures (p. 131).

The working temperature is about 500° and the pressure 100–250 atm. in the **Haber process** (1905) and up to 1000 atm. in the **Claude process.**

The catalyst is generally pure iron mixed with " promoters " (p. 143) such as molybdenum or (usually) potassium and aluminium oxides, and iron nitride is

probably formed as an intermediate product (p.144). The gas mixture is circulated by pumps through the catalyst in strong chrome-steel pressure vessels (Fig. 242) with internal heat exchangers, the heat of reaction maintaining the temperature of the catalyst. The ammonia formed is either absorbed in water under pressure in the Haber process or liquefied by cooling in the Claude process. The argon in the atmospheric nitrogen used is blown off from time to time with some $N_2 + 3H_2$ mixture.

The percentages of ammonia by volume *in equilibrium* conditions are given in the table (Larson and Dodge, *J.A.C.S.*, 1924, **46**, 367). When the plant is working at an economical rate the gas does not remain in contact with the catalyst long enough for equilibrium to be reached, and the conversions are always smaller than these.

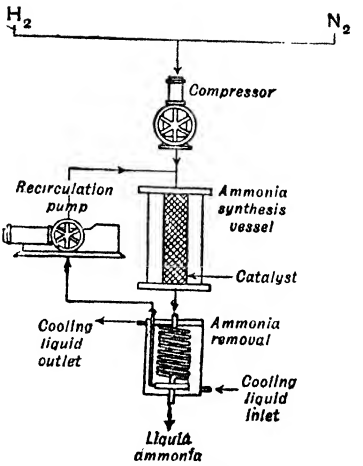


FIG. 242.—Synthetic ammonia apparatus (diagrammatic).

Pressure	10	100	300	600	1000 atm.
400° C.	3·85	25	47	65	80
450	2·1	16·5	36	54	70
500	1·2	10·6	26·4	42	57 5
550	0·76	6·8	19	32	41
600	0·5	4·5	14	23	31·5
700	0·23	2·2	7·3	12·6	13

The *nitrogen* is prepared by the fractionation of liquid air (p. 654), the *hydrogen* (p. 283) :

(i) by electrolysis of water ;
(ii) from water gas and steam ;
(iii) by liquefying more condensible gases from coke-oven gas by cooling.

The mixture $N_2 + 3H_2$ is also made directly from a mixture of producer gas (N_2 and CO), water gas (H_2, CO and CO_2), and steam by passing over a catalyst, when the reaction $CO + H_2O \rightleftharpoons CO_2 + H_2$ occurs. The carbon dioxide is removed by solution in water at 25 atm. pressure and the residual carbon monoxide in ammonical cuprous formate solution at 250 atm. pressure, and the gas is dried before passing to the ammonia catalyst.

The ammonia may be converted into ammonium sulphate by the calcium sulphate process (p. 321), or into ammonium chloride by the ammonia-soda process (pp. 307, 318).

In the **cyananide process** for making ammonia (Rothe ; Frank and Caro, 1899) atmospheric nitrogen is passed over crushed calcium carbide electrically heated at 1100° by carbon rods inside drums of carbide. In a modified process a mixture of powdered carbide with some calcium chloride or fluoride is raked continuously through a furnace heated by electric arcs. A mixture of calcium cyanamide $CaCN_2$ and graphite is formed as a dark grey mass called " cyanamide " or " nitrolim " : $CaC_2 + N_2 = CaCN_2 + C$.

Calcium cyanamide is a derivative of **cyanamide** $C{\equiv}N{-}NH_2$, the amide of cyanic acid CN·OH in which OH is replaced by NH_2.

The crystal structure of $CaCN_2$ is entirely analogous to that of sodium azide NaN_3 (p. 560), with a hexagonal lattice (Bredig, *J.A.C.S.*, 1942, **64**, 1730). Free cyanamide $CN{\cdot}NH_2$ is formed by the action of ammonia on cyanogen bromide CN·Br.

Powdered calcium cyanamide is agitated with cold water to decompose unchanged carbide and then stirred with water and a little sodium carbonate in a pressure digester or autoclave, into which steam is blown to a pressure of 3–4 atm. The pressure rises to 12–14 atm. owing to formation of ammonia gas, which is blown off with some steam to condensers, the ammonia solution formed being heated with steam in a still to drive out ammonia gas: $CaCN_2 + 3H_2O = CaCO_3 + 2NH_3$.

Ground calcium cyanamide is also used directly as a fertiliser, when ammonia is formed in the soil. If the crude product is fused in an electric furnace with a little salt, calcium cyanide is formed: $CaCN_2 + C = Ca(CN)_2$.

Hydroxylamine

Hydroxylamine NH_2OH, discovered by Lossen in 1865, is ammonia in which a hydrogen atom is replaced by hydroxyl. It is a base and with acids forms salts by addition of a proton to form the **hydroxylaminium** cation $NH_3(OH)^+$, *i.e.* ammonium with H replaced by OH. *E.g.* $NH_2OH + HCl = NH_3(OH)Cl$. The salts are sometimes formulated as NH_2OH,HCl, etc., and called "hydroxylamine hydrochloride", etc. The salts are obtained by:

(1) The reduction of nitric oxide by nascent hydrogen (Ludwig and Hein, 1869): $NO + 3H = NH_2OH$.

Nitric oxide is bubbled through flasks containing granulated tin, concentrated hydrochloric acid, and a few drops of platinic chloride solution to deposit platinum on the tin and form a galvanic couple. Hydroxylaminium chloride is formed and usually some ammonium chloride (Divers and Haga, *J.C.S.*, 1885, **47**, 623, say ammonium chloride is not formed in complete absence of air). The tin is precipitated with hydrogen sulphide and the filtrate evaporated to dryness. The solid is extracted first with cold and then boiling absolute alcohol, which dissolves the $NH_3(OH)Cl$ but not NH_4Cl. Hydroxylaminium chloride is then precipitated from the alcohol solution by ether.

Hydroxylamine is formed by adding dilute nitric acid to zinc and dilute sulphuric acid evolving hydrogen (Divers, etc., *J.C.S.*, 1883, **43**, 447; 1885, **47**, 597).

(2) The reduction of ethyl nitrate by nascent hydrogen (Lossen, 1865): $C_2H_5NO_3 + 6H = NH_2OH + C_2H_5OH + H_2O$.

Thirty g of $C_2H_5NO_3$, 120 g. of granulated tin and 40 g. of HCl (s. g. 1·12) are mixed, when reaction occurs spontaneously. The solution is treated as in (1).

(3) The electrolytic reduction of nitric acid (Tafel, 1902; Schoch and Pritchett, *J.A.C.S.*, 1916, **38**, 2042): $HNO_3 + 6H = NH_2OH + 2H_2O$.

A cooled cylindrical lead anode is separated by a porous pot from an amalgamated lead beaker serving as a cathode, the whole being cooled in ice. Fifty p.c. sulphuric acid is placed in each compartment, and 50 p.c. nitric acid is added drop by drop to the cathode compartment. Hydroxylaminium sulphate $(NH_3OH)_2SO_4$ is formed in 80 p.c. yield. By precipitation with barium chloride, hydroxylaminium chloride is formed.

(4) The interaction of nitrites and acid sulphites in solution (Raschig, 1887; Divers and Haga, *J.C.S.*, 1896, **69**, 1665; Semon, *J.A.C.S.*, 1923, **45**, 188; Rollefson and Oldershaw, *ibid.*, 1932, **54**, 977).

The reaction occurs in three stages, the sodium salts of *hydroxylamine disulphonic acid* and *hydroxylamine monosulphonic acid* being formed as intermediate stages:

$$(a) \quad NaNO_2 + 3NaHSO_3 = HO{\cdot}N(SO_3Na)_2 + Na_2SO_3 + H_2O$$

$$(b) \quad HO{\cdot}N(SO_3Na)_2 + H_2O = HO{\cdot}NH(SO_3Na) + NaHSO_4$$

$$(c) \quad HO{\cdot}NH(SO_3Na) + H_2O = HO{\cdot}NH_2 + NaHSO_4.$$

EXPT. 9.—Sulphur dioxide is *slowly* passed into a concentrated solution of 2 mols of commercial $NaNO_2$ and 1 mol of Na_2CO_3 at $-2°$, with good stirring, until just acid. The solution, containing sodium hydroxylamine disulphonate, is warmed with a few drops of dilute sulphuric acid, when hydrolysis to sodium hydroxylamine monosulphonate occurs. It is then kept at 90°–95° for two days, when hydrolysis to hydroxylaminium sulphate $(NH_3OH)_2SO_4$ occurs. It is neutralised with sodium carbonate, evaporated to small bulk, and cooled, when Glauber's salt $Na_2SO_4{,}10H_2O$ crystallises. The filtrate on further evaporation deposits hydroxylaminium sulphate, which is quickly recrystallised from water.

Anhydrous hydroxylamine was prepared by Lobry de Bruyn (1891) by adding a solution of sodium methoxide in methyl alcohol (obtained by dissolving sodium in the alcohol) to a solution of hydroxylaminium chloride in methyl alcohol, filtering off the sodium chloride, and distilling under reduced pressure (40 mm.), when methyl alcohol first distils and then hydroxylamine:

$$NH_3(OH)Cl + CH_3ONa = NH_2OH + CH_3OH + NaCl.$$

It also crystallises on cooling the filtered solution to $-18°$ (Lecher and Hofmann, 1922).

Crismer (1890) prepared the compound of hydroxylamine with zinc chloride $ZnCl_2{,}2NH_2OH$ by boiling zinc oxide with hydroxylaminium chloride solution and distilled it at 120°, either alone or mixed with aniline. Uhlenluth (1900) heated hydroxylaminium phosphate at 135° under 13 mm. pressure:

$$(NH_3OH)_3PO_4 = 3NH_2OH + H_3PO_4.$$

Pure hydroxylamine forms colourless, odourless, very deliquescent scales or hard rhombic needles, s. g. 1·35, m.p. 33°. It may be distilled under reduced pressure (55°–58°/22 mm.) but explodes when heated at ordinary pressure. The vapour explodes at 60°–70° in contact with air. The vapour density corresponds with the formula NH_2OH. The solid slowly decomposes above 15°, evolving nitrogen, ammonia, and nitrous oxide; solutions containing up to

60 p.c. of NH_2OH, although fairly stable, slowly decompose in a similar way :

$$3NH_2OH = N_2 + NH_3 + 3H_2O$$
$$4NH_2OH = N_2O + 2NH_3 + 3H_2O.$$

The solution is a weaker base than ammonia :

$$NH_2OH + H_2O \rightleftharpoons NH_3OH^{\cdot} + OH'$$

and precipitates hydroxides of many metals (Al, Zn, etc.). The salts are hydrolysed.

Ordinary **hydroxylaminium chloride** is $(NH_3OH)Cl$, but compounds of this with 1 and 2 NH_2OH and similar salts with the bromide and iodide are known. The ordinary **hydroxylaminium sulphate** is $(NH_3OH)_2SO_4$, which forms alums (replacing alkali sulphates) : there is an acid sulphate $(NH_3OH)HSO_4$.

Although hydroxylamine combines with some salts, *e.g.* $ZnCl_2$, it shows much less tendency to do this than ammonia and does not combine with copper and silver salts.

Hydroxylamine and its salts are *powerful reducing agents*, precipitating cuprous oxide from alkaline copper solution (Fehling's solution) and gold from its salts, and reducing ferric to ferrous salts in acid solution. In these reactions nitrous oxide is formed, perhaps by way of hyponitrous acid :

$$2NH_2OH + 2O = HO{\cdot}N{=}N{\cdot}OH + 2H_2O = N_2O + 3H_2O$$
$$2NH_2OH + 4CuO = N_2O + 3H_2O + 2Cu_2O$$
$$2NH_2OH + 4FeCl_3 = N_2O + 4FeCl_2 + 4HCl + H_2O$$

With nitrous acid or nitrites it evolves nitrous oxide :

$$NH_2OH + HO{\cdot}NO = HO{\cdot}N{=}N{\cdot}OH + H_2O = N_2O + 2H_2O.$$

Iodine solution in presence of sodium bicarbonate oxidises hydroxylamine quantitatively (Bray, etc., *J.A.C.S.*, 1919, **41**, 1363) :

$$2NH_2OH + 2I_2 = N_2O + 4HI + H_2O.$$

On heating with nitric acid nitric oxide is evolved (cf. NH_4NO_3) :

$$NH_2OH + HNO_3 = 2NO + 2H_2O.$$

In *alkaline* solution hydroxylamine *oxidises* ferrous hydroxide to ferric hydroxide and is itself reduced to ammonia :

$$NH_2OH + 2Fe(OH)_2 + H_2O = NH_3 + 2Fe(OH)_3.$$

In absence of water hydroxylamine can act as a very feeble acid : with lime it gives $HOCa{\cdot}O{\cdot}NH_2$ and with calcium $(H_2NO)_2Ca$, both explosive on heating. Fulminic acid $C{\equiv}N{\cdot}OH$ on boiling with hydrochloric acid gives hydroxylamine. A neutral solution of a hydroxylamine salt with sodium nitroprusside and a little alkali hydroxide gives a red colour on heating (test).

Nitrogen Halides

Nitrogen forms *trihalides* NX_3 with fluorine, chlorine and iodine, and possibly with bromine. These may be regarded as halogen substitution products of ammonia, and the intermediate stages NH_2X and NHX_2 are known

for chlorine and bromine and possibly fluorine. The common " nitrogen iodide " is NI_3NH_3.

Nitrogen trifluoride NF_3 is a colourless rather inert gas, m.p. −216·6°, b.p. −119°, obtained by the electrolysis of fused acid ammonium fluoride NH_4HF_2; with more HF, small amounts of NH_2F, NHF_2 and perhaps NF_2 are also formed. A mixture of NF_3 and hydrogen explodes when kindled: $2NF_3 + 3H_2 = N_2 + 6HF$ (Ruff and Staub, 1928).

Nitrogen trichloride NCl_3 was obtained in 1811 as a yellow explosive oil by the action of chlorine on a solution of ammonium chloride by Dulong, who lost an eye and three fingers by an explosion. He gave it the formula NCl_3. An abstract of his research was published by Thenard and Berthollet in 1813. Davy's analysis in 1813 gave more chlorine than corresponds with NCl_3, but the latter formula was found in 1834 by Balard, who prepared the compound by the action of hypochlorous acid on an ammonium salt. Kolbe (1847) found that NCl_3 separates at the anode in the electrolysis of ammonium chloride solution.

Since nitrogen chloride is formed by the action of excess of chlorine on anhydrous ammonia, with or without an anhydrous solvent (CCl_4 or pentane), the reaction is probably (W. A. Noyes, *J.A.C.S.*, 1920, **42**, 2167, 2173):

$$NH_3 + 3Cl_2 = NCl_3 + 3HCl,$$

and the reactions with ammonium salts are, *e.g.*

$$NH_4Cl + 3Cl_2 \rightleftharpoons NCl_3 + 4HCl$$
$$NH_4Cl + 3HOCl \rightleftharpoons NCl_3 + HCl + 3H_2O.$$

In the preparation of NCl_3 (V. Meyer, *Ber.*, 1888, **21**, 26) a flask of chlorine is inverted over a freshly prepared 25 p.c. solution of ammonium chloride, a lead saucer being placed under the mouth of the flask (Fig. 243). The chlorine is absorbed and oily drops of nitrogen trichloride float on the solution. These fall into the lead saucer, which should be removed when a little liquid has collected. If a little turpentine is passed by a long pipette into the flask, covered by a strong box, a violent explosion results, the flask being shattered. The drop of oil in the dish explodes violently when touched with a feather dipped in turpentine. According to Noyes, ammonium sulphate solution gives better results than the chloride. *These experiments are dangerous.*

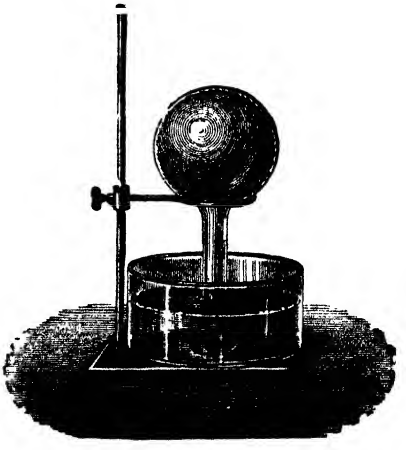


FIG. 243.—Preparation of nitrogen trichloride.

Nitrogen trichloride is a yellow volatile oil, s. g. 1·65, b.p. 71°, which does not freeze at −40° (Davy). The vapour has an irritating smell and attacks the

eyes. The liquid explodes by shock, at 100°, in direct sunlight, and in contact with phosphorus, many oils (including turpentine), fused potassium hydroxide, rubber, phosphine, nitric oxide, etc.

When chlorination is complete, the oil has the formula NCl_3 (Gattermann, *Ber.*, 1888, **21** 751; Chapman and Vodden, *J.C.S.*, 1909, **95**, 138). It was analysed by decomposition with ammonia: $NCl_3 + 4NH_3 = N_2 + 3NH_4Cl$, and precipitating the chloride with silver nitrate; the p.c. of chlorine found was 89·1, whilst NCl_3 requires 89·17.

A solution of nitrogen chloride in benzene is prepared *with specified precautions* by acidifying a solution of bleaching powder with hydrochloric acid, adding ammonium chloride, and shaking with benzene (Hentschel, *Ber.*, 1897, **30** 1434, 1792, 2642).

Monochloramine NH_2Cl is formed when ammonia and sodium hypochlorite in equimolecular amounts react in solution: the liquid is distilled in vacuum, the vapour dried with potassium carbonate, and condensed in liquid air: $NaOCl + NH_3 = NH_2Cl + NaOH$. It forms colourless crystals, melting at −66° and decomposing at higher temperature (Raschig, 1907—solution; Marckwald and Wille, 1923—solid).

Dichloramine $NHCl_2$ is formed in solution by the action of chlorine on a solution of ammonium sulphate buffered to an acidity of pH 4·5 to 5, when it is the sole product, and also by acidification of monochloramine solution. It can be extracted by chloroform (Chapin, *J.A.C.S.*, 1929, **51**, 2112).

Nitrogen bromide.—Millon (1838) by the action of potassium bromide solution on NCl_3 obtained a red explosive oil which he supposed was **nitrogen tribromide** NBr_3, but it was not analysed.

A purple-red compound $NBr_3{,}6NH_3$ is formed by cooling to −95° a mixture of bromine vapour and excess of ammonia at 20° and 1–2 mm. pressure (Schmeisser, 1940). **Monobromamine** NH_2Br and **dibromamine** $NHBr_2$ are said to be formed in solution by the action of bromine on ammonia in dry ether (Moldenhauer and Burger, 1929).

Nitrogen iodide.—Courtois (1812) by the action of ammonia solution on iodine obtained a black explosive powder, which was shown by Gay-Lussac and by Davy (1814) to contain nitrogen and iodine. Gladstone (1851–54) formulated it NHI_2; Gay-Lussac, and Stahlschmidt (1863) regarded it as NI_3, and Bunsen (1852) by mixing alcoholic solutions of ammonia and iodine obtained a compound $NI_3{\cdot}NH_3$: $2NH_3 + 3I_2 = NI_3NH_3 + 3HI$. Szuhay (1893) by suspending nitrogen iodide in water and adding ammoniacal silver nitrate solution obtained a black explosive powder which he formulated $NAgI_2$, and hence supposed that nitrogen iodide is NHI_2.

That Bunsen's formula for nitrogen iodide is correct was proved by Chattaway (*J.C.S.*, 1896, **69**, 1572, *Amer. Chem. J.*, 1900, **23**, 363; 1900, **24**, 138, 342). He showed that the product of the action of ammonia on iodine is a dark red crystalline compound NI_3NH_3, and confirmed the observation of Selivanov (1894) that hypoiodous acid is the first product of the action, this reacting with more ammonia to form nitrogen iodide:

(*a*) $NH_4OH + I_2 = NH_4I + HOI$

(*b*) $NH_3 + HOI = NH_4OI$

(*c*) $3NH_4OI \rightleftharpoons NI_3NH_3 + NH_4OH + 2H_2O$.

EXPT. 10.—Triturate *gently* 1 g. of iodine with conc. ammonia in a glass mortar, filter the black nitrogen iodide, and tear the filter paper into small pieces which are allowed to dry spontaneously on a piece of cardboard, the pieces being well separated. If a dry portion is touched with a feather tied to a stick it explodes sharply and violet fumes of iodine are evolved: $8NI_3NH_3 = 5N_2 + 9I_2 + 6NH_4I$. If two portions are close together and one is exploded, the shock may explode the other.

EXPT. 11.—Add a solution of iodine in potassium iodide drop by drop to concentrated ammonia in a test-tube. The precipitate at first redissolves to a clear liquid giving the reactions of hypoiodous acid, *e.g.* a brown pp. with $MnSO_4$ sol. Further addition of iodine gives a black pp. of nitrogen iodide, but this redissolves in a large excess of conc. ammonia, showing that reaction (*c*) above is reversible.

Nitrogen iodide oxidises sulphites to sulphates, arsenites to arsenates, etc., each atom of iodine having the oxidising effect of an atom of oxygen, as in hypoiodous acid HOI (Chattaway and Stevens, *Amer. Chem. J.*, 1900, **23**, 369). *E.g.* with sodium sulphite the reaction is:

$$NI_3NH_3 + 3Na_2SO_3 + 3H_2O = 3Na_2SO_4 + 2NH_4I + HI.$$

The free acid may be titrated with baryta and the iodide with silver nitrate and the composition determined. Silberrad (*J.C.S.*, 1905, **87**, 55) confirmed the formula by the action of zinc ethyl:

$$NI_3NH_3 + 3Zn(C_2H_5)_2 = 3ZnC_2H_5I + NH_3 + N(C_2H_5)_3.$$

He showed that Szuhay's compound is $NI_3 \cdot AgNH_2$.

Nitrogen tri-iode NI_3 is obtained by the action of gaseous ammonia on $KIBr_2$, and remains as a black residue on quickly washing with water (Cremer and Duncan, *J.C.S.*, 1930, 2750): $KIBr_2 \rightleftharpoons KBr + IBr$; $3IBr + 4NH_3 = NI_3 + 3NH_4Br$.

HYDRAZINE

Hydrazine was prepared by Curtius in 1887 from organic compounds and was obtained by Raschig in 1907 by the action of sodium hypochlorite on ammonia solution in the presence of a little glue or gelatin, without which hydrazine is not formed. Monochloramine is first formed and then reacts with the ammonia in excess to form hydrazine:

(1) $NH_3 + NaOCl = NH_2Cl + NaOH$; (2) $NH_3 + NH_2Cl = N_2H_4 + HCl$.

The reaction indicates that the structure of hydrazine is $H_2N \cdot NH_2$, diamide.

EXPT. 12.—Prepare a solution of sodium hypochlorite by passing 4 g. of chlorine into 100 c.c. of 5 p.c. NaOH cooled in a freezing mixture and expose to air for 12 hours to remove excess of chlorine. Add to 200 c.c. of saturated ammonia to which 15–20 c.c. of 1 p.c. gelatin solution has been added. Boil to half the

volume, cool, and add a mixture of 10 c.c. conc. H_2SO_4 and 50 c.c. of water and then alcohol till slightly cloudy. On cooling, hydrazinium sulphate $(N_2H_5)HSO_4$ crystallises. Filter in a Buchner funnel and dry on a porous plate (Joyner, *J.C.S.*, 1923, **123**, 1141 ; Henrion, *Chem. Abstr.* (Brit.), 1934, 498A).

If hydrazine sulphate is distilled under reduced pressure with concentrated potash solution with a condenser without rubber or cork connections, a colourless fuming liquid, b.p. 119°, or 47°/26 mm., is obtained. This is called " hydrazine hydrate " but is a solution of maximum boiling point. The solution may be concentrated to 95 p.c. by distilling with xylene, which carries over the water. When hydrazine hydrate is distilled with its own weight of caustic soda in small pieces, **anhydrous hydrazine** passes over at 150° as a liquid which on cooling solidifies to colourless crystals, m.p. 1·4°, b.p. 113·5°. Anhydrous hydrazine may also be prepared from hydrazinium chloride and sodium methoxide in a similar way to anhydrous hydroxylamine (p. 553).

Hydrazine and the hydrate readily absorb moisture and carbon dioxide from the air, are freely soluble in water and alcohol, and are poisonous. Anhydrous hydrazine inflames in dry oxygen, reacts readily with halogens: $2I_2 + N_2H_4 = 4HI + N_2$, explodes in contact with potassium permanganate, sets free ammonia from ammonium chloride, and decomposes on heating: $3N_2H_4 = N_2 + 4NH_3$. It dissolves sulphur, selenium, phosphorus and arsenic, and sodium forms a deep blue solution. By the action of sodium in absence of oxygen, a crystalline solid $H_2N{\cdot}NHNa$ is obtained, which explodes violently in presence of oxygen or moisture.

Hydrazine, a very weak base, forms two series of salts which can be regarded as containing the *hydrazinium* cation $N_2H_5^{\cdot}$. The chlorides are N_2H_4,HCl or $(N_2H_5)Cl$ and $N_2H_4,2HCl$ or $(N_2H_6)Cl_2$. The ordinary sulphate is N_2H_4,H_2SO_4 or $(N_2H_5)HSO_4$ and the normal sulphate is $(N_2H_5)_2SO_4$. The salts are hydrolysed in solution. Double salts, *e.g.* $ZnCl_2,N_2H_4,2HCl$, are known.

Hydrazine and its salts are powerful *reducing agents*. Gold, silver and platinum are precipitated from their salts ; alkaline copper solution is reduced on warming to cuprous oxide: $4CuO + N_2H_4 = 2Cu_2O + 2H_2O + N_2$, or to copper ; ferric salts are reduced to ferrous salts, and iodates to iodides:

$$3N_2H_4 + 2IO_3' = 3N_2 + 2I' + 6H_2O.$$

In its reducing actions hydrazine is converted into water and nitrogen: $N_2H_4 + 2O = 2H_2O + N_2$.

EXPT. 13.—To 25 c.c. of 0·5 p.c. copper acetate solution in a clean test-tube add ammonia until a clear dark blue solution is formed. Add three drops of hydrazine hydrate and heat the colourless solution of cuprous compound in a beaker of water at 90°. A bright copper mirror forms on the tube (Chattaway, 1908).

Hydrazine may be determined by titration with iodine in presence of sodium bicarbonate: $N_2H_4 + 2I_2 = 4HI + N_2$, or with permanganate in presence of dilute sulphuric acid: $N_2H_4 + 2O = 2H_2O + N_2$.

Hydrazoic Acid

Hydrazoic acid or *azoimide* (HN_3 or $NH{\cdot}N_2$), obtained by Curtius in 1890 from organic compounds, is formed by the careful oxidation of hydrazine with nitric acid (Sabanajeff, 1899) or hydrogen peroxide (Tanatar, 1902): $3N_2H_4 + 5O = 2HN_3 + 5H_2O$.

Expt. 14.—Warm 1 g. of hydrazine sulphate with 4 c.c. of nitric acid of s. g. 1·3 in a test-tube and lead the vapour by a bent tube into silver nitrate solution. A white curdy precipitate of **silver azide** AgN_3 is formed. This is dangerously explosive when dry and should be disposed of by dissolving in ammonia, in which it is soluble (cf. AgCl). **Lead azide** $Pb(N_3)_2$ is used as a detonator instead of mercury fulminate.

Hydrazoic acid is formed by the decomposition of hydrazinium nitrite under special conditions: $(N_2H_5)NO_2 = HN_3 + 2H_2O$ (cf. $NH_4NO_2 = N_2 + 2H_2O$). Thus hydrazine reacts with ethyl or amyl nitrite and alkali to form an azide, and silver azide is precipitated when hydrazine is added to saturated silver nitrite solution. Sodium azide is formed on fusing sodamide with sodium nitrate (Browne and Wilcoxon, *J.A.C.S.*, 1926, **48**, 682):

$$3NaNH_2 + NaNO_3 = NaN_3 + 3NaOH + NH_3,$$

and potassium azide by the reaction:

$$3KNH_2 + KNO_3 = KN_3 + 3KOH + NH_3$$

in liquid ammonia in a sealed tube at 90° (Franklin, *J.A.C.S.*, 1934, **56**, 568).

Hydrazoic acid is formed by the action of hydrazine on a solution of nitrogen trichloride in benzene: $N_2H_4 + NCl_3 = HN_3 + 3HCl$, and by oxidising a mixture of hydrazine and hydroxylamine with chromic acid or hydrogen peroxide:

$$N_2H_4 + NH_2OH + 2O = HN_3 + 3H_2O.$$

Active nitrogen forms azides with sodium, potassium, rubidium and caesium; with sodium a nitride Na_3N is first formed (Wattenberg, 1930).

Hydrazoic acid was first prepared from inorganic materials by Wislicenus (1892), by heating sodamide in a stream of nitrous oxide:

$$NaNH_2 + N_2O = NaN_3 + H_2O,$$

the water formed reacting with excess of sodamide to form ammonia:

$$NaNH_2 + H_2O = NaOH + NH_3.$$

Sodamide is made by passing dry ammonia gas over sodium fused in porcelain boats in a hard glass tube heated at 150°–250°:

$$2Na + 2NH_3 = 2NaNH_2 + H_2.$$

The ammonia is then displaced by a current of dry nitrous oxide and the tube heated at 190°. When no more ammonia is evolved the tube is cooled and the pumice-like mass of NaN_3 and NaOH is distilled with excess of dilute sulphuric acid, when a solution of hydrazoic acid HN_3 comes over. The solution is fractionated and finally distilled over fused calcium chloride, when anhydrous hydrazoic acid is formed (cf. Dennis and Isham, *J.A.C.S.*, 1907, **29**, 18).

Anhydrous hydrazoic acid is a colourless mobile liquid, b.p. 37°, m.p. −80°, with a nauseous smell. *It is a very dangerously poisonous and explosive substance*, and may detonate violently on heating. It forms with water a corrosive acid solution in which only about 1 p.c. is ionised: $HN_3 \rightleftharpoons H^{\cdot} + N_3'$. The solution readily dissolves many metals (zinc, iron, copper, etc.) with evolution of nitrogen and the formation of azides; ammonia and a trace of hydrazine are formed, but hydrogen is not evolved, except a little with magnesium (Franklin, *J.A.C.S.*, 1934, **56**, 568). It reacts quantitatively with nitrous acid: $HN_3 + HNO_2 = N_2 + N_2O + H_2O$.

The alkali metal and barium azides evolve pure nitrogen on heating: $2NaN_3 = 2Na + 3N_2$. Azides of heavier metals are explosive. The soluble azides give a blood-red colour with ferric chloride, resembling thiocyanate but discharged by hydrochloric acid; with silver nitrate they give a white curdy precipitate of silver azide AgN_3, soluble in ammonia, and exploding at 250°. The ammonia and hydrazine salts, NH_4N_3 or N_4H_4, and $(N_2H_5)N_3$ or N_5H_5, are formed by neutralisation; they are colourless and crystalline.

The vapour density of hydrazoic acid corresponds with HN_3. The correct structural formula was first given by Thiele as $N{\equiv}N{=}NH$, which is written in modern form as $N{\leftarrow}N{=}NH$, corresponding with the electronic structure $\overset{\times\,\times}{N}\,\overset{\times}{\cdot}\,:N::\overset{\cdot\,\cdot}{N}\circ H$, and the N_3 group in the salts and esters is linear; in the esters the radical R is inclined to the line of the N_3 group. The structure is established by X-ray and other methods and the old cyclic formula proposed by Curtius must be abandoned (Hendricks and Pauling, *J.A.C.S.*, 1925, **47**, 2904; Frevel, *ibid.*, 1936, **58**, 779; Buswell, etc., *ibid.*, 1939, **61**, 2809; Eyster, *J. Chem. Phys.*, 1940, **8**, 135). The electronic formulae of the azide and cyanate ions and neutral nitrous oxide are very similar:

$$[\overset{\cdot\,\cdot}{N}::N::\overset{\cdot\,\cdot}{N}]' \qquad [\overset{\cdot\,\cdot}{N}::C::\overset{\cdot\,\cdot}{O}]' \qquad \overset{\cdot\,\cdot}{N}::N::\overset{\cdot\,\cdot}{O}$$

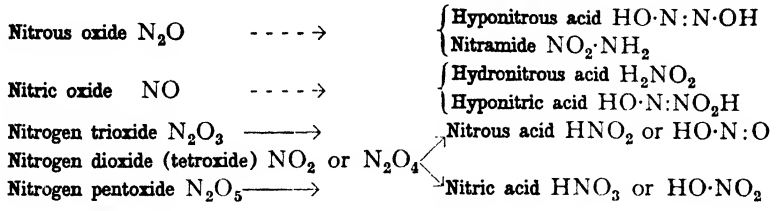
The SCN group is also linear (Cowley and Partington, *J.C.S.*, 1932, 2825).

Chlorine azide ClN_3 is a colourless very explosive gas formed by the action of sodium hypochlorite and boric acid on sodium azide solution (Raschig, 1908); **iodine azide** IN_3 is an explosive pale yellow solid obtained by the action of iodine on silver azide (Hantzsch, 1900); **cyanogen azide** $(CN\,N_3)_2$ is a white crystalline solid formed from cyanogen bromide and sodium azide (Darzens, 1913; Hart, *J.A.C.S.*, 1928, **50**, 1922); and **sulphuryl azide** $N_3{\cdot}SO_2{\cdot}N_3$ is a liquid formed from sulphuryl chloride SO_2Cl_2 and sodium azide (Curtius and Schmidt, 1922–25). The curious **azido-dithiocarbonic acid** $N_3{\cdot}CS{\cdot}SH$, formed by addition of carbon disulphide and hydrazoic acid: $S{=}C{=}S + N_3 - H = N_3{\cdot}CS{\cdot}SH$, gives a yellow precipitate with copper salts; ferric chloride oxidises it to a very explosive compound, probably $N_3{\cdot}CS{\cdot}S{\cdot}S{\cdot}CS{\cdot}N_3$ (Sommer, 1915; Browne and Hoel, *J.A.C.S.*, 1922, **44**, 2106, 2315).

Oxides and Oxyacids of Nitrogen

In the following table a full arrow shows that the compound on the right is formed by the action of water on that on the left; a broken arrow shows that

the second substance is not formed by direct hydration but may be regarded only formally as a hydrate :



An unstable **higher oxide** of uncertain formula, perhaps NO_3, and an acid which may be **pernitric acid** HNO_4 or HO·O·NO_2 or **pernitrous acid** O:N·O·OH (isomeric with nitric acid) are also described.

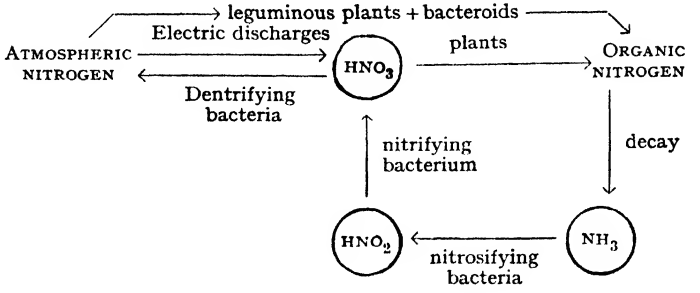
Nitrogen and oxygen react above 1000°, *e.g.* on sparking or in an electric arc, to form nitric oxide as a primary product : $N_2 + O_2 \rightleftharpoons 2NO$. In presence of excess of oxygen, the nitric oxide on cooling forms red nitrogen dioxide : $2NO + O_2 = 2NO_2$, which at lower temperatures partly polymerises into tetroxide : $2NO_2 \rightleftharpoons N_2O_4$. With water this reacts to form nitrous and nitric acids : $2NO_2 + H_2O = HNO_2 + HNO_3$. Nitrous acid is unstable and decomposes, forming partly nitrogen trioxide which colours the solution blue : $2HNO_2 \rightleftharpoons N_2O_3 + H_2O$, and partly nitric acid and nitric oxide which is evolved : $3HNO_2 = HNO_3 + 2NO + H_2O$. In presence of excess of oxygen, the nitric oxide reoxidises, and finally nearly all the nitric oxide may be converted into nitric acid.

EXPT. 15,—Pass sparks between platinum electrodes through dry air in a glass globe. After a time the gas becomes yellowish from formation of NO_2, and reddens litmus solution on shaking. The formation of an acid on sparking air in presence of water was noticed by Priestley in 1779 (see Meldrum, *J.C.S.*, 1933, 902) ; Cavendish (1785) showed it was nitric acid.

THE NITROGEN CYCLE

Nitric acid is formed by electrical discharges in the atmosphere and is washed down by rain ; about 250,000 tons are said to be formed in 24 hours. Leguminous plants convert atmospheric nitrogen into organic compounds by the agency of micro-organisms (*Pseudomonas radicocola*) which occur in nodules called *bacteroids* on the roots. Algae, fungi, and mosses also assimilate free nitrogen, and a bacterium, *Azotobacter chröococcum*, present in soil, fixes elementary nitrogen in presence of calcium carbonate. The organic nitrogen compounds formed by plants serve as food for herbivorous animals, and the proteins of the latter are utilised by carnivora. When plants and animals die and decay, ammonia is formed. In the soil this is oxidised by *nitrosifying bacteria* to nitrites, and these by the *nitrifying bacterium* to nitrates, the latter again serving as nourishment for plants. A few plants can assimilate nitrogen from ammonium compounds and some from nitrites. Part of the fixed nitrogen

in the soil is set free by *denitrifying bacteria.* A diagram of the " nitrogen cycle " is given below :



NITRIC ACID

The composition of nitric acid was first established by Cavendish in 1785. He passed electric sparks through a mixture of air and oxygen over mercury in an inverted V-tube also containing some potash solution, wires from an electrical machine and condenser dipping into the mercury in the cups (Fig. 244). The oxides of nitrogen formed dissolved in the alkali, forming a solution of potassium nitrate and nitrite. After absorbing the excess of oxygen by a solution of potassium sulphide (liver of sulphur), only a small bubble remained (probably argon). Thus nitric acid contains nitrogen and oxygen.

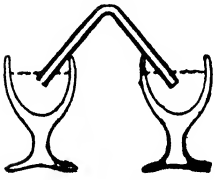


FIG. 244.—Cavendish's experiment.

Nitric acid is formed when a suitable mixture of detonating gas ($2H_2 + O_2$) and air is exploded by a spark. If the volume of air is more than twice that of the detonating gas, the temperature of the explosion is too low to form nitric acid, and no acid is formed on exploding a mixture of hydrogen and air (Cavendish, 1781 ; Bunsen, 1857). A hydrogen flame burning in oxygen containing some nitrogen forms nitric oxide and nitric acid (Kolbe, 1861).

Nitric acid (*aqua fortis*) was first made (apparently about 1100 A.D.) by distilling nitre or saltpetre, KNO_3, with copperas (ferrous sulphate, $FeSO_4,7H_2O$) (Guttmann, *J.S.C.I.*, 1901, **20**, 5). Glauber, about 1658, made the fuming acid (*spiritus nitri Glauberi*) by distilling nitre with concentrated sulphuric acid. Equimolecular amounts of potassium (or sodium) nitrate and concentrated sulphuric acid are distilled in a glass retort :

$$KNO_3 + H_2SO_4 = KHSO_4 + HNO_3.$$

Some nitric acid vapour is decomposed by heat : $4HNO_3 = 4NO_2 + 2H_2O + O_2$, and the red NO_2 dissolves in the condensed acid, colouring it yellow.

EXPT. 16.—Add 49 g. (26 c.c.) of concentrated sulphuric acid to 50 g. of potassium nitrate in a stoppered retort, stir with a glass rod, heat on wire gauze and collect the nitric acid in a cooled receiver. Notice the red gas at the

beginning and end. The acid is yellow. Add a piece of copper foil to it: the metal does not usually dissolve. Add a few drops of water: the copper dissolves and red fumes are evolved (Andrews, 1837).

Nitric acid may be concentrated by distillation with concentrated sulphuric acid. *Pure nitric acid* is difficult to make: the concentrated acid may be redistilled on a water-bath under reduced pressure in a current of ozonised oxygen (Veley and Manley, *Phil. Trans.*, 1898, **191**, 365); or the 98 p.c. acid may be frozen, when colourless crystals, m.p. $-41{\cdot}3°$, separate. The pure acid is a colourless liquid, s.g. 1·522 at 14°. Both liquid and vapour are slightly dissociated at the ordinary temperature: $2HNO_3 \rightleftharpoons N_2O_5 + H_2O$, and more at higher temperatures, and pure anhydrous liquid HNO_3 does not seem capable of existence. A current of dry air passed through the liquid removes the volatile N_2O_5 and acid containing 98·62 p.c. HNO_3 remains.

The purest acid begins to boil at 78·2° at atm. pressure but decomposes; when three-quarters have distilled the residue is 95·8 p.c. HNO_3; on further distillation a maximum b.p. acid (120·5°; 68 p.c. HNO_3; see p. 60) is formed; this remains as a residue in the retort when weaker solutions are distilled. The composition corresponds roughly with $2HNO_3,3H_2O$, but it is not a definite hydrate, since Roscoe (1861) showed that the composition varies with the distillation pressure. Two definite solid hydrates, HNO_3,H_2O (m.p. $-38°$) and $HNO_3,3H_2O$ (m.p. $-18{\cdot}5°$) are known.

Nitric acid vapour is decomposed by light: on exposure of a half-filled bottle the nitrogen dioxide formed dissolves and renders the liquid yellow. The liquid in a completely filled bottle remains colourless (Scheele, 1772; Reynolds and Taylor, *J.C.S.*, 1912, **101**, 131). The yellow acid is decolorised by warming to 60°–80° and bubbling dry air through it.

A yellow *fuming nitric acid*, containing oxides of nitrogen and used as an oxidising agent, is prepared by distilling nitre and sulphuric acid with a little starch, which reduces some nitric acid to N_2O_4.

On mixing nitric acid and water heat is evolved and there is a contraction which is a maximum at the composition $3HNO_3 + H_2O$.

The densities in g./c.c. at 15° of mixtures of nitric acid and water are (cf. Bousfield, *J.C.S.*, 1915, **107**, 1405):

Density	HNO_3 p.c.	Density	HNO_3 p.c.	Density	HNO_3 p.c.
1·050	8·99	1·250	39·82	1·450	77·28
1·100	17·11	1·300	47·49	1·500	94·09
1·150	24·84	1·350	55·79	1·510	98·10
1·200	32·36	1·400	65·30	1·520	99·67

Nitric acid is a strong monobasic acid: $HNO_3 \rightleftharpoons H^{\cdot} + NO_3'$, and its salts, the **nitrates**, are obtained by the action of the acid on metals (when oxides of nitrogen, not hydrogen, are usually evolved), oxides, hydroxides, or carbonates. A few acid nitrates, *e.g.* NH_4NO_3,HNO_3 and $NH_4NO_3,2HNO_3$ are known (Groschuff, 1903). Alkali nitrates on heating form oxygen and nitrites: $2KNO_3 = 2KNO_2 + O_2$; ammonium nitrate gives nitrous oxide: $NH_4NO_3 = N_2O + 2H_2O$; heavy metal nitrates form oxides, nitrogen dioxide

and oxygen: *e.g.* $2Pb(NO_3)_2 = 2PbO + 4NO_2 + O_2$. Most nitrates are soluble in water; some basic nitrates (*e.g.* of lead and bismuth) are insoluble.

Nitric acid is a powerful oxidising agent and is itself reduced to oxides of nitrogen. Hot concentrated nitric acid oxidises iodine to iodic acid, phosphorus to phosphorous and phosphoric acids (white phosphorus may cause an explosion), sulphur to sulphuric acid, arsenious oxide to arsenic acid. Tin is oxidised in the cold to hydrated stannic oxide. Burning charcoal burns brilliantly on the concentrated acid, and heated sawdust is inflamed by it. Oil of turpentine explodes with very concentrated nitric acid and evolves black clouds of carbon. Alcohol is violently oxidised, sometimes with explosion. Hydrogen sulphide is not oxidised by the pure acid but in presence of nitrogen oxides it decomposes with separation of sulphur (see p. 696). Stannous chloride in hydrochloric acid is oxidised to stannic chloride and the nitric acid reduced to hydroxylamine and ammonia.

Ferrous salts reduce nitric acid to nitric oxide which in the cold dissolves in the excess of ferrous salt to a black solution which evolves nitric oxide on heating:

$$6FeSO_4 + 2HNO_3 + 3H_2SO_4 = 3Fe_2(SO_4)_3 + 2NO + 4H_2O,$$

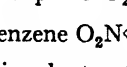
or

$$6Fe^{\cdot\cdot} + 2NO_3' + 8H^{\cdot} = 6Fe^{\cdot\cdot\cdot} + 2NO + 4H_2O.$$

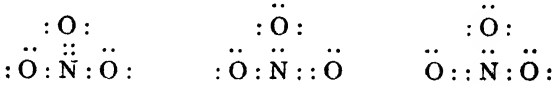
This is the basis of the well-known "ring test" for nitrates: ferrous sulphate is dissolved in the solution in a test-tube and concentrated sulphuric acid carefully added. A black (purple in the sulphuric acid) ring forms at the junction of the liquids.

Other tests for nitric acid and nitrates are: (i) the red colour with a solution of brucine in concentrated sulphuric acid; (ii) the deep blue colour with a solution of diphenylamine in concentrated sulphuric acid; (iii) the evolution of red oxides of nitrogen on heating with concentrated sulphuric acid and copper turnings; (iv) *nitron* reagent (1 p.c. in 5 p.c. acetic acid) forms a white crystalline precipitate of nitron nitrate $C_{20}H_{16}N_4.HNO_3$, on adding 5 drops of reagent and 1 drop of dilute sulphuric acid to 5 c.c. of nitrate solution.

The structure of nitric acid is best represented as a molecule with two forms in resonance (p. 269):

The symmetrical nature of the nitro-group $—NO_2$ is shown by the absence of a dipole moment (p. 276) in *p*-dinitrobenzene O_2N  NO_2.

The *nitrate ion* has an equilateral triangle structure with the N to O distance 1·21A. (Elliott, *J.A.C.S.*, 1937, **59**, 1380), and may be represented as a resonance structure of three forms (Pauling, *The Nature of the Chemical Bond*, 1940, 209):



the carbonate ion being similar, with C in place of N and hence two negative charges instead of one and the C to O distance 1·31A. $NaNO_3$ and $CaCO_3$ are isomorphous.

In presence of concentrated sulphuric acid (a dehydrating agent) in *nitration reactions* nitric acid behaves as if it has the structure $HO{\cdot}NO_2$, *e.g.*

$$C_6H_6 + HO{\cdot}NO_2 = C_6H_5{\cdot}NO_2 + H_2O.$$

The action of nitric acid on metals.—Nearly all metals, except platinum, rhodium, iridium, tantalum and gold are attacked by dilute or concentrated nitric acid. Tin, arsenic, antimony, tungsten and molybdenum are converted into oxides but the remaining metals form nitrates. Aluminium is scarcely attacked by cold nitric acid; iron and chromium become " passive " in the concentrated acid and lead is covered with a protective film of nitrate. During the reactions part of the acid is reduced to the oxides NO_2, NO and N_2O, and free nitrogen, hydroxylamine and ammonia. The products depend on the metal, temperature, concentration of acid, and the presence of the products of reaction. Hydrogen is evolved only by magnesium or manganese with cold 1 or 2 p.c. nitric acid.

H. E. Armstrong and Acworth (*J.C.S.*, 1877, **32**, 54; Bancroft, *J. Phys. Chem.*, 1924, **28**, 475, 973; Milligan, *ibid.*, 544, 794; Joss, *ibid.*, 1926, **30**, 60; Hedges, *J.C.S.*, 1930, 561) suggested that the *primary reaction* in *all* cases is the liberation of nascent hydrogen: $M + HNO_3 = MNO_3 + H$. (Hot concentrated hydrochloric, hydrobromic and hydriodic acids dissolve copper with evolution of hydrogen.) The nascent hydrogen reduces the nitric acid and further reactions occur:

Secondary reactions, probably proceeding in definite stages:

(*a*) $HNO_3 + 2H = HNO_2$ (nitrous acid) $+ H_2O$

(*b*) $2HNO_3 + 8H = H_2N_2O_2$ (hyponitrous acid) $+ 4H_2O$

(*c*) $HNO_3 + 6H = NH_2O$ (hydroxylamine) $+ 2H_2O$

(*d*) $HNO_3 + 8H = NH_3$ (ammonia) $+ 3H_2O$

Tertiary reactions, in which the secondary products interact:

(1) *decomposition* into simpler compounds:

(*a*) $3HNO_2 = HNO_3 + 2NO$ (nitric oxide) $+ H_2O$

(*b*) $2HNO_2 = N_2O_3$ (nitrous anhydride) $+ H_2O$

(*c*) $H_2N_2O_2 = N_2O$ (nitrous oxide) $+ H_2O$

(2) *double decomposition*:

(*a*) $HNO_2 + NH_3 = N_2$ (nitrogen) $+ 2H_2O$

(*b*) $HNO_2 + NH_2O = N_2O + 2H_2O$.

(*c*) $HNO_2 + HNO_3 = 2NO_2 + H_2O$.

The action on *copper* may be represented as follows:

$$3Cu + 6HNO_3 = 3Cu(NO_3)_2 + 6H$$
$$6H + 3HNO_3 = 3HNO_2 + 3H_2O$$
$$3HNO_2 = HNO_3 + 2NO + H_2O$$

$\therefore$ by addition: $3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 2NO + 4H_2O$.

According to Divers (*J.C.S.*, 1883, **43**, 443, 455), some metals, *e.g.* Ag, Cu, Bi, Hg, give nitric oxide but no hydroxylamine or ammonia ; other metals, *e.g.* Fe, Zn, Sn, Cd, Mn, Mg, give NH_3, or NH_3O, and N_2O. He thought metals of the first group do not reduce the acid below the stage of nitrous acid, which gives nitric oxide as a secondary product, but those of the second form hydrogen which reduces the excess of acid.

The product depends on the concentration and temperature of the acid (concentrated nitric acid gives mainly nitrogen dioxide with copper :

$$Cu + 4HNO_3 = Cu(NO_3)_2 + 2NO_2 + 2H_2O),$$

and on the accumulation of the salt in the solution, since the prolonged action of dilute nitric acid on copper gives nitrogen and nitrous oxide. Nitrous oxide is evolved with zinc (p. 574).

Millon (1842) and Veley (*Proc. Roy. Soc.*, 1890, **48**, 458 ; *J.S.C.I.*, 1891, **10**, 204) showed that *pure* nitric acid in the absence of nitrous acid scarcely acts on copper, silver, bismuth or mercury ; other metals react in the absence of nitrous acid but more slowly than when it is present. Since nitrous acid is formed the speed of the reaction increases as it proceeds.

EXPT. 17.—Take three pieces of clean copper foil and immerse them in three glasses containing (*a*) 50 c.c. of 50 p.c. nitric acid (1 : 1) ; (*b*) 50 c.c. of acid + 5 c.c. of hydrogen peroxide (20 vols.) ; (*c*) 50 c.c. of acid + 1 c.c. of hydrazine hydrate. The copper in (*a*) is at once violently attacked ; that in (*b*) and (*c*) remains for a time without change. The hydrogen peroxide oxidises nitrous acid : $HNO_2 + H_2O_2 = HNO_3 + H_2O$, whilst hydrazine decomposes it.

According to Millon and Veley nitric oxide is a primary product, formed from traces of nitrous acid ; a green solution of copper nitrite is formed which is then decomposed by nitric acid to reproduce nitrous acid :

$$Cu + 4HNO_2 = Cu(NO_2)_2 + 2H_2O + 2NO.$$
$$Cu(NO_2)_2 + 2HNO_3 = Cu(NO_3)_2 + 2HNO_2 ;$$
$$HNO_3 + H_2O + 2NO \rightleftharpoons 3HNO_2.$$

The nitric oxide reduces nitric acid to nitrous acid, and nitric oxide is evolved only at a certain concentration of nitrous acid. Nitrous acid may be formed by electrolysis (" local action ") caused by impurities in a metal.

The manufacture of nitric acid.—Concentrated nitric acid is made by distilling sodium nitrate with concentrated sulphuric acid in an iron retort. The materials are taken in the ratio for the reaction :

$$3NaNO_3 + 2H_2SO_4 = Na_2SO_4 + NaHSO_4 + 3HNO_3.$$

One or two tons of previously dried sodium nitrate (Chile nitre) are heated with rather more than this weight of 93 p.c. sulphuric acid in a large cast-iron pot uniformly heated in a brickwork furnace (Fig. 245). Nitric acid *vapour* does not attack iron, which is corroded by the liquid acid. The acid is condensed in some type of cooler : vitreous silica spirals cooled in water, stoneware U-tubes or horizontal glass tubes cooled partly by air and water, S-shaped tubes of

silicon iron, or large stoneware Woulfe's bottles. The oxides of nitrogen also formed are absorbed by water in a tower : $4NO_2 + O_2 + 2H_2O = 4HNO_3$.

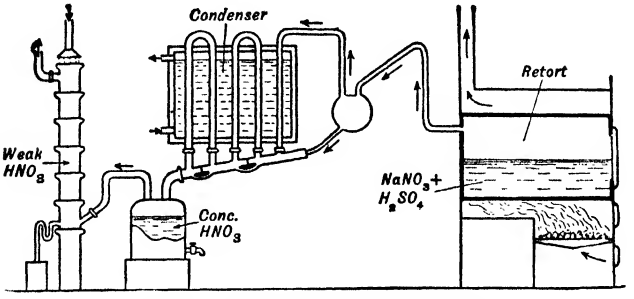


FIG. 245.—Manufacture of nitric acid.

In the **Valentiner process** (1891) the apparatus is air-tight and a vacuum is maintained by an air-pump. The distillation under reduced pressure (25 cm.) takes place at a lower temperature (100°–150°), so that there is less decomposition, and the reaction occurs more rapidly.

The liquid residue in the retort is run out and allowed to solidify ; it is a mixture or compound of about equimolecular proportions of $NaHSO_4$ and Na_2SO_4 and is called *nitre cake*. The retort process is now little used.

The arc process.—The union of atmospheric nitrogen and oxygen at the high temperature of the electric arc was demonstrated by Crookes in 1892 and a small experimental plant was worked at Manchester in 1899. As carried out from 1902 in Norway at Notodden and Rjukan, the *Birkeland and Eyde process* utilised 350,000 horse-power from water-power, but it is now replaced by ammonia synthesis and oxidation of ammonia.

Air is drawn through the flat circular furnace (Fig. 246) in which an alternating current electric arc burning between water-cooled copper poles is spread out by an electromagnet into an *apparent* disc, the temperature of which is 3000°. In this flame combination of oxygen and nitrogen occurs : $N_2 + O_2 \rightleftharpoons 2NO$. At 3000° the equilibrium yield of NO is 5 p.c. by volume ; at 1500° it is only 0·4 p.c. Since the reaction absorbs heat the yield is greater at higher temperatures (p. 134).

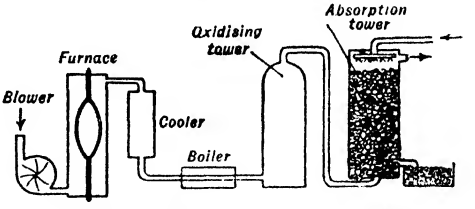


FIG. 246.—Diagram of the arc process.

The gas after rapid cooling to "freeze" the equilibrium leaves the furnace at 1000°, containing 1 p.c. of NO, passes through iron pipes lined with brick to the firebox of a tubular boiler, where it is cooled to 150° with production of steam in the boiler, and then passes through large aluminium pipes exposed to the air where it cools to 50°.

When the furnace gas has cooled below 600° nitrogen dioxide begins to form : $2NO + O_2 \rightleftharpoons 2NO_2$; this reaction is somewhat slow, since it is termolecular, and to give time the gas passes through a large empty iron oxidising

tower and then to three or four gigantic absorption towers, 65–80 ft. high and 18 ft. diameter, built of granite slabs and packed with broken quartz over which water is circulated. In these towers nitric acid is formed (p. 561):

$$2NO_2 + H_2O \rightleftharpoons HNO_2 + HNO_3$$
$$3HNO_2 \rightleftharpoons HNO_3 + 2NO + H_2O.$$

The NO is reoxidised by the excess of air present, forming NO_2, which re-enters the reaction. Nearly all the nitrous acid is so removed from the solution, and 30 p.c. nitric acid runs from the first tower, the acid being pumped from the last tower through all the towers in succession.

The dilute nitric acid is either neutralised with limestone to form calcium nitrate, which is evaporated and exported as a fertiliser ("Norge saltpeter"), or is concentrated by distilling it with concentrated sulphuric acid under reduced pressure.

When the gas becomes very dilute, oxidation of NO is very slow, and a mixture of NO and NO_2 passes from the last absorption tower, about 85 p.c. of the oxides of nitrogen having by this time been absorbed. This gas passes into an iron tower packed with quartz, down which a solution of sodium carbonate trickles, which absorbs nearly all the residual oxides to form chiefly sodium nitrite with some nitrate: $NO + NO_2 + Na_2CO_3 = 2NaNO_2 + CO_2$.

The oxidation of ammonia.—Nitric acid is now mostly made by the catalytic oxidation of synthetic ammonia. In 1788 the Rev. Isaac Milner, President of Queens' College, Cambridge, found that ammonia gas passed over heated manganese dioxide is oxidised to nitr.c oxide. Kuhlmann, of Lille, in 1839 found that ammonia is oxidised to nitric oxide by passing it mixed with air over a heated platinum catalyst: $4NH_3 + 5O_2 = 4NO + 6H_2O$.

EXPT. 18.—Pass a current of air through ammonia in a wash-bottle and the mixed gas over a roll of platinum foil heated to dull redness in a hard glass tube. Notice the formation of red gas and white fumes in a globe attached to the tube.

The process was first used technically by Ostwald in 1902 but has since been much improved. The best results are obtained when the gas passes very rapidly over the catalyst; with a slow current much free nitrogen is formed. A mixture of 1 vol. of purified ammonia gas and 7·5 vols. of air filtered from dust and preheated to about 500° in a counter-current apparatus (cf. p. 707) is passed through a converter (Fig. 247) containing two fine platinum (or platinum-rhodium) gauzes in contact, when the exothermic reaction proceeds automatically. More than 90 p.c. of the ammonia is oxidised to nitric oxide, and 1 sq. ft. of double catalyst will produce 1½ tons of HNO_3 in 24 hours. By rapidly cooling the oxidised gas much of the steam may be condensed from it before the nitric oxide is oxidised. More air is then added and the mixture sent to an oxidation tower and absorption towers in which it is treated with water to form nitric acid from the NO_2 produced by the oxidation of the NO (p. 561). The rate of conversion is much greater with a mixture of ammonia and oxygen, $NH_3 + 2O_2$, with sufficient steam to render it non-explosive, and nitric acid

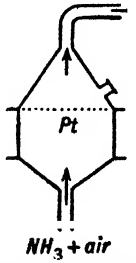


FIG. 247.—Ammonia oxidation converter.

may then be obtained directly by cooling the gas from the converter. The gas from the converter when air is used contains NO, nitrogen, and excess of air. It is cooled and passed into packed stainless steel towers through which water circulates. Formation of nitric acid occurs as in the arc process. The cooled gas may also be compressed by pumps into stainless steel tanks containing water. Modern processes aim at converting ammonia and oxygen (which is obtained as a by-product in ammonia synthesis) into nitric acid.

On passing the cooled oxidised gas through milk of lime, calcium nitrate and nitrite are formed: $2Ca(OH)_2 + 2N_2O_4 = Ca(NO_3)_2 + Ca(NO_2)_2 + 2H_2O$. When all the lime is neutralised, nitric acid is formed by reactions previously explained. This decomposes the nitrite into nitrate and oxides of nitrogen which are fully oxidised to NO_2 by air and passed into another absorber of milk of lime: $Ca(NO_2)_2 + 2HNO_3 = Ca(NO_3)_2 + NO + NO_2 + H_2O$.

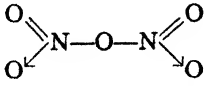
If ammonia gas mixed with air is blown into the cooled and fully oxidised gas from the oxidation apparatus, solid ammonium nitrate is deposited as a powder: $4NO_2 + O_2 + 2H_2O + 4NH_3 = 4NH_4NO_3$.

Nitrogen pentoxide or nitric anhydride N_2O_5 was obtained by Deville (1849) by the action of chlorine on silver nitrate: $4AgNO_3 + 2Cl_2 = 4AgCl + 2N_2O_5 + O_2$. It is best prepared by dehydrating concentrated nitric acid by phosphorus pentoxide (Weber, 1872; Daniels and Bright, *J.A.C.S.*, 1920, **42**, 1131): $2HNO_3 + P_2O_5 = N_2O_5 + 2HPO_3$.

Pure concentrated nitric acid, freshly distilled over concentrated sulphuric acid, is placed in a stoppered retort cooled in a freezing mixture and pure phosphorus pentoxide in slight excess added in small quantities. The mixture is distilled at as low a temperature as possible in a current of ozonised oxygen, the gas passed through a phosphorus pentoxide tube, and pure crystals of N_2O_5 are obtained by cooling in solid carbon dioxide and ether.

Crystalline nitrogen pentoxide is also formed by passing ozonised oxygen into cooled liquid nitrogen tetroxide (Helbig, 1902): $N_2O_4 + O_3 = N_2O_5 + O_2$.

Nitrogen pentoxide forms white very hygroscopic crystals, stable below 0° but slowly decomposing and becoming yellow at ordinary temperature even in sealed tubes: $2N_2O_5 = 2N_2O_4 + O_2$. They sublime on warming and if not quite pure melt with decomposition at 29·5° to a dark brown liquid, which decomposes into NO_2 and oxygen at 50°. If suddenly heated the crystals explode. They dissolve with a hissing noise in water forming nitric acid: $N_2O_5 + H_2O = 2HNO_3$. Phosphorus and potassium burn in the liquid if slightly warmed; charcoal does not decompose it even on boiling but burns brilliantly if previously kindled. Sulphur forms white vapours, condensing to crystals of nitrosyl disulphate, $S_2N_2O_9$ (p. 581). A crystalline compound, $N_2O_5,2HNO_3$, m.p. 5°, is formed on cooling a solution of the anhydride in concentrated nitric acid. The formula of nitrogen pentoxide is (see p. 564):



Halides of nitric acid.—When OH in nitric acid $HO{\cdot}NO_2$ is substituted by fluorine or chlorine the compounds NO_2F and NO_2Cl are formed, the group NO_2 being called *nitryl*.

Nitryl fluoride NO_2F is a very reactive gas, b.p. $-72{\cdot}4°$, m.p. $-166°$, formed by the action of nitric oxide on excess of fluorine at the temperature of liquid oxygen (Moissan and Lebeau, 1905; Ruff, etc., 1932): $4NO + F_2 = 2NO_2F + N_2$.

Pernitryl fluoride NO_2F is a colourless explosive gas, b.p. $-42°$, formed by the action of fluorine on concentrated nitric acid or solid potassium nitrate (Cady, *J.A.C.S.*, 1934, **56**, 2635; Yost and Beerbower, *ibid.*, 1935, **57**, 782). It is a powerful oxidising agent: $NO_3F + 2KI = KNO_3 + KF + I_2$. With concentrated alkali it evolves oxygen: $2NO_3F + 4KOH = O_2 + 2KF + 2KNO_3 + 2H_2O$, but with dilute alkali it forms fluorine monoxide: $2NO_3F + 2NaOH = F_2O + 2NaNO_3 + H_2O$.

Nitryl chloride NO_2Cl is a colourless gas, b.p. $-15°$, m.p. $-145°$, formed by the action of ozone on nitrosyl chloride (Schumacher and Sprenger, 1929): $NOCl + O_3 = NO_2Cl + O_2$, and in small amount by other reactions, *e.g.* $4NO_2 + 3HCl = 2NOCl + NO_2Cl + HNO_3 + H_2O$ (Müller, 1862; W. A. Noyes, *J.A.C.S.*, 1932, **54**, 3615). It is stable at 100° but decomposes at higher temperatures: $2NO_2Cl = 2NO_2 + Cl_2$.

Nitryl perchlorate $NO_2(ClO_4)$ (Gordon and Spinks, *Canad. J. Res.*, 1940, **18**, 358) is a white crystalline solid formed by mixing ozonised air with chlorine dioxide. It decomposes rapidly at 120° and with water forms nitric and perchloric acids.

Nitric Oxide

Although nitric oxide was obtained by van Helmont, Mayow, Hales and Cavendish, it was first recognised as a distinct gas by Priestley (1772), who prepared it by the action of copper or mercury on dilute nitric acid and called it *nitrous air*: $3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 2NO + 4H_2O$.

Expt. 19.—Copper turnings are placed in a flask and a mixture of equal volumes of concentrated nitric acid and water poured on. The gas is collected over water. It is not very pure and especially in the later stages of the reaction contains variable amounts of nitrogen and nitrous oxide. It may be purified by passing into cold saturated ferrous sulphate solution; a nearly black liquid is formed containing $FeSO_4{\cdot}NO$, which on gentle heating evolves *nearly* pure nitric oxide. The gas so purified contains 1/500 of its volume, probably nitrous oxide, not absorbed by fresh ferrous sulphate.

Nearly pure nitric oxide may be obtained by heating a mixture of potassium nitrate, ferrous sulphate, and dilute sulphuric acid (Pelouze, 1848): $6FeSO_4 + 2HNO_3 + 3H_2SO_4 = 3Fe_2(SO_4)_3 + 2NO + 4H_2O$, by heating a solution of ferrous chloride in concentrated hydrochloric acid with sodium nitrate: $3FeCl_2 + NaNO_3 + 4HCl = 3FeCl_3 + NaCl + 2H_2O + NO$, and by dropping concentrated sulphuric acid on sodium nitrite covered with 3–4 times its weight of water (Guye and Davila, 1905; W. A. Noyes, *J.A.C.S.*, 1925, **47**, 2170): $3NaNO_2 + 3H_2SO_4 = 3NaHSO_4 + HNO_3 + 2NO + H_2O$.

Very *pure nitric oxide* is obtained (W. Crum, 1847) by shaking mercury with concentrated sulphuric acid to which nitric acid or a nitrate has been

added, and passing the gas over solid potash to remove any nitrogen dioxide · $2HNO_3 + 6Hg + 3H_2SO_4 = 2NO + 3Hg_2SO_4 + 4H_2O$.

This reaction is used in the estimation of nitrites or nitrates, or oxides of nitrogen in commercial sulphuric acid, in the Lunge *nitrometer* (Fig. 248). This consists of a graduated tube *A* with a stopcock *B* communicating with a small cup *C* through which the substance is admitted, an outlet tube *D*, and a levelling tube *E*. The tube *A* is filled with mercury and the substance admitted from *C* through *B*. Concentrated sulphuric acid is then introduced and the mixture shaken violently with the mercury The volume of nitric oxide is read off.

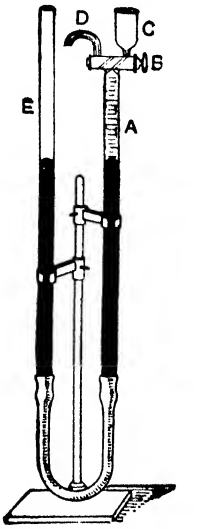


FIG. 248.—Lunge's nitrometer.

Pure nitric oxide is also obtained by dropping a solution of sodium nitrite and potassium ferrocyanide into dilute acetic acid (Van Deventer, 1893):

$$Fe(CN)_6'''' + NO_2' + 2H^{\cdot} = Fe(CN)_6''' + NO + H_2O,$$

and by the action of sodium nitrite solution on an acidified solution of potassium iodide (Winkler, 1901; Johnston and Giauque, *J.A.C.S.*, 1929, **51**, 3194):

$$2NO_2' + 2I' + 4H^{\cdot} = I_2 + 2NO + 2H_2O.$$

The pure gas should be collected over mercury as it acts slightly on water, evolving traces of nitrous oxide: $4NO + H_2O = N_2O + 2HNO_2$.

Nitric oxide is a colourless gas, slightly heavier than air (normal density 1·3402 g./lit.) and sparingly soluble in water. The volumes at S.T.P. absorbed by 1 vol. of water are:

	0°	15°	30°	60°
Vols. of NO - -	0·074	0·051	0·040	0·0295

It is not easily liquefied: the liquid, s. g. 1·269 at the b.p. −151·7°, is somewhat darker blue than liquid oxygen, it freezes at −163·6° to a solid of the same colour; the critical temperature is −96°, the critical pressure 64 atm.

Nitric oxide is freely soluble in cold ferrous sulphate solution forming a black liquid, observed by Priestley. This contains an unstable compound of ferrous sulphate and nitric oxide which is readily decomposed on heating, with evolution of nitric oxide.

The maximum absorption corresponds with $FeSO_4 \cdot NO$ but the reaction is reversible, the absorption depending on temperature, concentration of the ferrous salt (other ferrous salts, *e.g.* $FeCl_2$, and cobalt, nickel, manganese, chromous and cuprous chlorides also absorb NO), pressure, and the presence of other salts: $FeSO_4 + NO \rightleftharpoons FeSO_4 \cdot NO$. Manchot (1906) regards the compound as $[Fe(NO)]SO_4 \rightleftharpoons Fe(NO)'' + SO_4''$, the nitric oxide being in the cation.

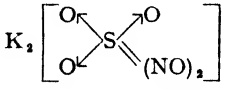
Compressed or liquid nitric oxide slowly decomposes into nitrous anhydride (which colours the liquid blue) and nitrous oxide (Briner, 1918): $4NO = N_2O_3 + N_2O$; this reaction also occurs very slowly in contact with water or alkali at ordinary pressure (Gay-Lussac, 1816; Russell and Lapraik, *J.C.S.*, 1877, **32**, 35).

Nitric oxide is slowly absorbed by acidified permanganate solution:

$$3MnO_4' + 5NO + 4H^{\cdot} = 3Mn^{\cdot\cdot} + 5NO_3' + 2H_2O.$$

It is not appreciably absorbed by alkali but readily dissolves in alkaline sulphite solution (which is the best absorbent for the gas), forming a **nitrososulphate**, *e.g.* $Na_2(NO)_2SO_3$.

The potassium salt $K_2(NO)_2SO_3$ crystallises when nitric oxide is passed over the surface of slightly alkaline potassium sulphite solution in a flask from which air is previously displaced by hydrogen (Davy, 1799; Pelouze, 1835). The nitrososulphates at once evolve nitrous oxide with acids: $K_2(NO)_2SO_3 = K_2SO_4 + N_2O$. The structure may resemble that of thiosulphates, two —NO radicals replacing =S:



Nitric oxide combines at room temperature with free oxygen to form nitrogen dioxide, the reaction being termolecular: $2NO + O_2 = 2NO_2$. The gases dried with phosphorus pentoxide do not react (H. B. Baker, *J.C.S.*, 1894, **65**, 611; 1929, 1661; cf. Smith, *J.A.C.S.*, 1943, **65**, 74). A green solid, said to be an oxide N_3O_4, is formed on passing nitric oxide into liquid oxygen, or by the action of air on solid nitric oxide at −180° (Hasche, *J.A.C.S.*, 1925, **47**, 2143).

Nitric oxide is the most stable oxide of nitrogen and begins to decompose into its elements appreciably only above 1000°. Unless this temperature is reached, combustion does not proceed in it. A burning taper, sulphur, charcoal and feebly burning phosphorus are extinguished, but brightly burning phosphorus continues to burn brilliantly in the gas, nitrogen and some NO_2 being formed along with P_2O_5. A mixture of nitric oxide and carbon disulphide vapour, made by shaking a few c.c. of carbon disulphide in a jar of the gas, when kindled burns with a brilliant blue flame (Berzelius, 1825).

A mixture of hydrogen and nitric oxide (or a higher oxide of nitrogen, or nitric acid vapour, but not nitrous oxide) when passed over heated platinum is reduced to ammonia: $2NO + 5H_2 = 2NH_3 + 2H_2O$.

Nitric oxide is absorbed by concentrated nitric acid to form a yellow solution of NO_2: $2HNO_3 + NO = 3NO_2 + H_2O$. With more dilute acid a green ($NO_2 + N_2O_3$) or blue (N_2O_3) solution is formed, but beyond a certain dilution (24 p.c.) the acid absorbs very little nitric oxide.

The *composition of nitric oxide* may be determined (Gay-Lussac and Thenard, 1811) by heating a piece of potassium (not sodium) in the dry gas confined over mercury in a bent tube (*College Course*, p. 487). A spiral of iron wire

may be strongly heated by an electric current in a cylinder of the gas over mercury. In both cases the oxygen is removed by the metal and *half* the volume of nitrogen remains: $2N_xO_y = N_2 +$ oxygen absorbed. Hence $x = 1$ and the formula is NO_y. The density gives the molecular weight 30, hence $y = 1$ and the formula is NO.

The reduction of nitric oxide by heated finely divided nickel was used to determine the atomic weight of nitrogen by R. W. Gray (*J.C.S.*, 1905, **87**, 1601): $2NO + 2Ni = N_2 + 2NiO$. The pure NO was prepared by subliming the solid. The gas was contained in a bulb *A* (Fig. 249) weighed first empty and then filled with gas. The platinum boat, heated electrically by a platinum spiral *H*, contained the nickel. After decomposition the nitrogen was removed from *A* and condensed in a weighed bulb *M* containing charcoal and cooled in liquid air. The increase in weight of *M* gave the weight of nitrogen, that of *A* the oxygen which combined with the nickel. The ratio N : O was 14·0085 : 16. The density of nitric oxide reduced (from the compressibility) to the ideal state (p. 11) gave the mol. wt. 30·009, ∴ N = 14·009. The accepted value is 14·008.

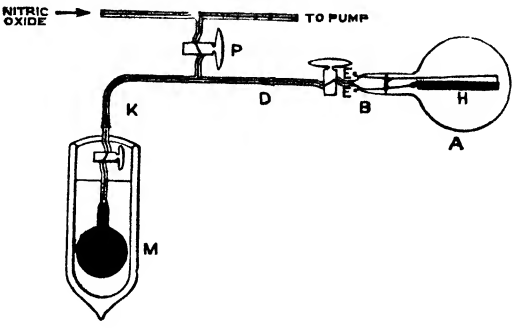


FIG. 249.—Gray's apparatus.

The nitric oxide molecule contains an odd electron and is paramagnetic. The electronic formula is perhaps best represented as a resonance hybrid (p. 270) of $:\dot{N}::\ddot{O}:$ and $:\ddot{N}::\dot{O}:$ with a three electron bond $:O::\dddot{N}:$ (Pauling, *J.A.C.S.*, 1931, **53**, 3225).

NITROUS OXID

Priestley in 1772 found that "nitrous air" (nitric oxide) exposed to iron or liver of sulphur (p. 313) contracts and the residual *diminished nitrous air* supports the burning of a taper better than common air, the flame being enlarged. Davy in 1799 prepared pure nitrous oxide by heating ammonium nitrate, a method discovered by Berthollet in 1785. Davy determined its composition and examined its physiological action. He called it *nitrous oxide*. Its use as an anaesthetic and its peculiar effects ("laughing gas") are well known. It does not support life, so that it is mixed with oxygen when breathed (*Everyday Chemistry*, p. 395).

Nitrous oxide is not easily synthesised but is formed by passing an electric discharge through nitrogen at low pressure in a fused silica tube, the walls of which have previously been saturated with oxygen by passing a discharge through that gas at low pressure in the tube (D. L. Chapman, Goodman, and Shepherd, *J.C.S.*, 1926, 1404).

Nitrous oxide is formed by the reduction of moist nitric oxide by sulphur dioxide or sulphites, or of nitric acid by metals or stannous chloride under special conditions :

$$2NO + SO_2 + H_2O = H_2SO_4 + N_2O$$
$$4Zn + 10HNO_3(\text{dilute}) = 4Zn(NO_3)_2 + 5H_2O + N_2O$$
$$2HNO_3 + 4SnCl_2 + 8HCl = 4SnCl_4 + 5H_2O + N_2O$$

A mixture of 1 vol. conc. H_2SO_4, 1 vol. conc. HNO_3 and 10 vols. of water is said to evolve fairly pure nitrous oxide with zinc (Schiff, *Annalen*, 1861, **118**, 84).

Nitrous oxide is conveniently prepared by the decomposition of ammonium nitrate by heat : $NH_4NO_3 = N_2O + 2H_2O + 5$ k. cal. If heated above 250° the salt is liable to explode by a strongly exothermic reaction (p. 320) ; before this occurs, nitric oxide, nitrogen and ammonia are evolved.

EXPT. 20.—Heat about 50 g. of ammonium nitrate, previously dried at 105°, in a plain retort over wire gauze. The salt melts at 170° when quite dry, usually at 165°, and begins to decompose below 200°. The gas is purified from higher oxides of nitrogen by passing through potassium permanganate solution, or potassium dichromate dissolved in dilute sulphuric acid, from chlorine (derived from ammonium chloride impurity in the nitrate) and nitric acid vapour by sodium hydroxide solution, and may be dried by concentrated sulphuric acid. It is collected over mercury, or by downward displacement. It may also be collected over warm water, but is then very moist. This gas contains a few p.c. of nitrogen. For use as an anaesthetic the carefully purified gas is liquefied by compression into steel cylinders.

Very pure nitrous oxide is evolved on mixing solutions of equimolecular amounts of hydroxylaminium chloride and sodium nitrite and warming gently if necessary (V. Meyer, 1875) : $NH_3(OH)^+ + NO_2^- = N_2O + 2H_2O$.

Nitrous oxide is a colourless gas, about 1½ times as heavy as air, normal density 1·9777 g./lit., with a faint sweetish odour and taste. It is appreciably soluble in water, and more soluble in alcohol. The volumes at S.T.P. absorbed are :

	0°	5°	10°	15°	20°	25°
1 vol. of water -	1·3052	1·0954	0·9196	0·7778	0·6700	0·5962
1 vol. of alcohol -	4·178	3·844	3·541	3·268	3·025	—

The solution has no action on litmus ; nitrous oxide is a neutral oxide and is not the true anhydride of hyponitrous acid $H_2N_2O_2$, although it is formed by its decomposition. At 0° and 10 atm. pressure a crystalline hydrate $N_2O,6H_2O$ is formed. When cooled to −90° or exposed to pressure (30 atm. at 0° ; 50 atm. at 15°) N_2O forms a colourless mobile liquid, b.p. −88·7° ; critical temperature 36·5°, critical pressure 71·66 atm., density of the liquid at b.p. 1·226 ; when cooled in liquid air or *rapidly* evaporated (not spontaneously on reducing the pressure, as in the case of liquid carbon dioxide) it forms a snow-like solid, with some transparent crystals, m.p. −90·8°.

Nitrous oxide supports combustion better than air, since it is easily decomposed by heat and forms a gas containing one-third its volume of oxygen, as compared with one-fifth in air : $2N_2O = 2N_2 + O_2$. (Nitric oxide forms a gas

containing half its volume of oxygen, but does not support combustion so easily as air or nitrous oxide since it is stable to about 1000°. Combustion in nitric oxide, once begun, is more brilliant than in nitrous oxide.) Decomposition of nitrous oxide begins at 520° and is complete at 900°. At lower temperatures the principal reaction is $2N_2O = 2N_2 + O_2$, but at 1300° the reaction $2N_2O = 2NO + N_2$ also occurs. It is decomposed by electric sparks and some nitric oxide is formed.

A taper burns in nitrous oxide with a brilliant flame, and charcoal burns, and a glowing chip is rekindled, as in oxygen. (The *dry* gas should be used.) Nitrous oxide is distinguished from oxygen by its smell, its greater solubility in water, and the fact that it does not produce a red gas with nitric oxide.

Brightly burning phosphorus burns in the gas with a brilliant flame, forming phosphorus pentoxide, nitrogen, and a little nitrogen dioxide. Feebly burning sulphur is extinguished, but brightly burning sulphur burns vigorously with a double flame. Sodium and potassium burn to oxides, and iron wire burns as in oxygen. A hydrogen flame is greatly enlarged in nitrous oxide. The ignition points of hydrogen, ethylene and propylene are lower in nitrous oxide than in oxygen or air (Dixon and Higgins, *Manch. Mem.*, 1927, **71**, 15).

Nitrous oxide is *endothermic* and is decomposed by the shock of exploding mercury fulminate. If mixed with detonating gas ($2H_2 + O_2$) it is completely decomposed on explosion.

Two vols. of nitrous oxide leave 3 vols. of gas (all the electrolytic gas forms liquid water), from which 1 vol. of oxygen is absorbed by alkaline pyrogallol, leaving 2 vols. of nitrogen. Thus $2N_xO_y = 2N_2 + O_2$, hence $x = 2$ and $y = 1$, and the formula is N_2O.

Gay-Lussac and Thenard (1811) determined the composition by heating potassium in the gas confined over mercury in a bent tube ; on cooling, an equal vol. of nitrogen remained, hence the gas contains its own volume of nitrogen, and the formula is N_2O_x. The density gives the mol. wt. 44, $\therefore x = 1$ and the formula is N_2O. The gas may also be decomposed by heated iron wire ; 1 vol. of nitrous oxide then gave 1·00686 vols. of nitrogen (Jaquerod and Bogdan, 1904), as it is more compressible than the latter.

Davy (1799) determined the composition of nitrous oxide by explosion with hydrogen. If 20 c.c. of nitrous oxide mixed with 20 c.c. of hydrogen are exploded in a eudiometer by a spark, 20 c.c. of nitrogen remain. The hydrogen will have combined with 10 c.c. of oxygen, hence 2 vols. of nitrous oxide are formed from 2 vols. of nitrogen and 1 vol. of oxygen, which shows that the formula is N_2O.

A mixture of *nitric* oxide and hydrogen does not usually explode when sparked, but the mixture $2NO + H_2$ is said to be exploded by a long intense spark (Cooke, *Chem. News*, 1888, **58**, 103, 130, 155). A mixture of 1 vol. of nitrous oxide, 1 vol. of nitric oxide and 2 vols. of hydrogen explodes when sparked and both the oxides are decomposed : $N_2O + NO + 2H_2 = 1\frac{1}{2}N_2 + 2H_2O$.

In an experiment 20 c.c. of nitrous oxide, 20 c.c. of nitric oxide, and 40 c.c. of hydrogen were exploded. Thirty c.c. of nitrogen remained. Of this, 20 c.c. must be derived from the nitrous oxide, hence the 20 c.c. of nitric oxide gave

30 – 20 = 10 c.c. of nitrogen. Again, 20 c.c. of hydrogen are used by the nitrous oxide, so that 40 – 20 = 20 c.c. of hydrogen have combined with the oxygen in the 20 c.c. of nitric oxide, which must therefore have been 10 c.c. Thus 20 c.c. of nitric oxide contain 10 c.c. of nitrogen and 10 c.c. of oxygen ; this corresponds with the formula NO.

The structure of nitrous oxide is well established : the molecule is linear and unsymmetrical (Langmuir, *J.A.C.S.*, 1919, **41**, 897 ; Pauling, *Proc. Nat. Acad. Sci.*, 1932, **18**, 294, 498) :

$$:\ddot{O}:\overset{\times}{\underset{\times}{N}}\overset{\times}{\underset{\times}{:}}\ddot{N}: \quad \text{or} \quad O{=}N{\rightarrow}N.$$

Nitrogen Trioxide or Nitrous Anhydride

Red vapours obtained by distilling diluted nitric acid with arsenious oxide or starch when cooled in a freezing mixture (Fig. 250) condense to deep blue volatile liquid nitrous anhydride :

$$As_2O_3 + 2HNO_3 + 2H_2O = N_2O_3 + 2H_3AsO_4$$
$$2C_6H_{10}O_5 + 18HNO_3 = 9N_2O_3 + 6(COOH)_2 + 13H_2O.$$

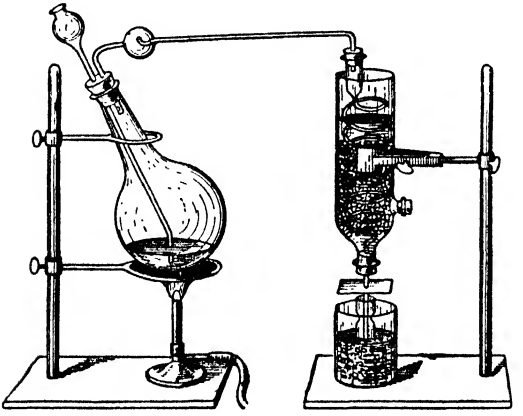


Fig. 250.—Preparation of nitrogen trioxide.

Expt. 21.—Heat 100 g. As_2O_3 and 80 c.c. of nitric acid of s. g. 1·35 (56 p.c.) in a flask with a paraffined cork connected with a glass worm cooled in ice and salt. Collect the blue liquid in a tube and seal off. *N.B.—Vapours of higher oxides of nitrogen are dangerously poisonous and great care should be taken not to inhale them.*

The red gas is rapidly absorbed by alkali hydroxide solution, forming nitrite, and by concentrated sulphuric acid, forming nitrososulphuric acid. It thus behaves as if it were nitrous anhydride N_2O_3 :

$$N_2O_3 + 2NaOH = 2NaNO_2 + H_2O$$
$$NO{\cdot}O{\cdot}NO + 2SO_2(OH)_2 = 2SO_2(OH){\cdot}O{\cdot}NO + H_2O.$$

The vapour density of the gas, however, corresponds with a mixture of equal volumes of NO and NO_2, and hence it was thought that N_2O_3 does not exist in the gaseous state : $N_2O_3 \rightleftharpoons NO + NO_2$. A small amount of undissociated N_2O_3, however, is present in the gas at room temperature : when the equilibrium mixture $N_2O_4 \rightleftharpoons 2NO_2$ is mixed with nitric oxide the expansion due to further dissociation of N_2O_4 on dilution with an indifferent gas is not observed.

Ramsay and Cundall (*J.C.S.*, 1885, **47**, 187, 672; 1890, **57**, 590) collected gaseous nitrogen dioxide in a tube over mercury, introduced a glass bulb filled with nitric oxide, and allowed the gases to mix by breaking the bulb. There was no change in volume, whilst it was assumed that there should have been a contraction if any N_2O_3 had been formed:

$NO + NO_2 = N_2O_3$ (contraction of $\frac{1}{2}$) or $2NO + N_2O_4 = 2N_2O_3$ (contraction of $\frac{1}{3}$).

Lunge and Porschnew (1894) avoided contact of nitrogen dioxide with mercury, which it attacks, by mixing the gases at 27·3° in a glass apparatus consisting of two bulbs connected by a tube with a glass diaphragm which could be broken by a marble. The apparatus was connected with a petroleum manometer. There was no contraction and in one experiment a slight expansion, which they attributed to dissociation of N_2O_4. They concluded that no N_2O_3 was formed.

Dixon and Peterkin (*J.C.S.*, 1899, **75**, 613; Abel and Proisl, *Z. Elektrochem.*, 1929, **37**, 712) pointed out that if there were no combination of NO and NO_2 in this experiment there would have been an expansion of nearly 10 c.c., owing to dilution and consequent increased dissociation: $N_2O_4 \rightleftharpoons 2NO_2$, the partial pressure of the N_2O_4 being reduced. Since they found a contraction of 0·3 c.c. some N_2O_3 must have been formed. With nitrogen dioxide and an indifferent gas, or with NO above 50°, there was the normal expansion of 10 c.c. The gas obtained by mixing 100 vols. of NO and 100 vols. of nitrogen dioxide (NO_2 and N_2O_4) at 27° they calculated should have the composition:

	N_2O_4	NO_2	NO	N_2O_3	Total
Before mixing	- 68	32	100	0	200
After mixing -	- 62	38	94	6	200

If the blue liquid is dried by prolonged exposure to phosphorus pentoxide it may be volatilised without decomposition and has a vapour density corresponding with N_4O_6, but in presence of the least trace of moisture the gas decomposes into NO and NO_2 (H. B. and M. Baker, *J.C.S.*, 1900, **77**, 647; 1907, **91**, 1862; D. L. Chapman, *ibid.*, 1937, 1991, could not repeat the experiments).

Liquid nitrous anhydride is obtained by the action of nitric oxide on solid nitrogen dioxide cooled by liquid air. It is not oxidised to nitrogen dioxide by oxygen below −100°, melts at −102°, and (unless quite dry) begins to decompose at −27° (Baume and Robert, *Compt. rend.*, 1919, **169**, 968).

The formula of nitrous anhydride is probably O=N·O·N=O; in spite of its intense colour the liquid is diamagnetic, and the molecule therefore does not contain an odd electron.

A mixture of nitric oxide with oxygen or air, made rapidly in presence of alkali, is quickly absorbed with formation of nitrite:

$$4NO + O_2 = 2NO + 2NO_2 \rightleftharpoons 2N_2O_3$$
$$N_2O_3 + 2KOH = 2KNO_2 + H_2O.$$

If the gas mixture is allowed to stand, it is less rapidly absorbed by alkali, and nitrite and nitrate are formed from the NO_2 produced by the complete oxidation of the nitric oxide (p. 582): $2NO_2 + 2KOH = KNO_2 + KNO_3 + H_2O$.

Potassium iodide solution absorbs only NO_2 from a mixture with NO: $2KI + 2NO_2 = 2KNO_2 + I_2$.

Nitrous Acid

Potassium or sodium nitrate when strongly heated melts and evolves oxygen, and a *nitrite* is formed (Scheele, 1774): $2KNO_3 = 2KNO_2 + O_2$. The reduction occurs at a lower temperature by fusing the nitrate with lead or copper; the nitrite is obtained by extracting with water, filtering from the metallic oxide and evaporating: $NaNO_3 + Pb = NaNO_2 + PbO$.

Alkali nitrites decompose at higher temperatures (Oswald, *Ann. Chim.*, 1914, **1**, 32):

$$3NaNO_2 = Na_2O + NaNO_3 + 2NO$$
$$5NaNO_2 = Na_2O + 3NaNO_3 + N_2$$

and the oxide formed dissolves as hydroxide. This dissolves lead oxide, which is precipitated by neutralising with nitric acid. The crystals of **sodium nitrite** formed on evaporation and dried at 50° have a yellowish colour and usually contain some nitrate. **Potassium nitrite** may be similarly obtained but does not crystallise well, hence it is precipitated from the solution by alcohol or is fused and cast into sticks.

Purer nitrites are formed by passing the red gas evolved on heating nitric acid with arsenious oxide (p. 576) into alkali solution (s. g. 1·38) or carbonate solution, out of contact with air:

$$2KOH + (NO + NO_2) = 2KNO_2 + H_2O$$
$$Na_2CO_3 + (NO + NO_2) = 2NaNO_2 + CO_2$$

and pure potassium nitrite by decomposing amyl nitrite with alcoholic potash:

$$C_5H_{11}NO_2 + KOH = C_5H_{11}OH \text{ (amyl alcohol)} + KNO_2.$$

Potassium and sodium nitrites are slightly, their concentrated solutions markedly, yellow. The solutions are not alkaline when the salts are pure. Sodium nitrite melts at 284°, and 4 parts dissolve in 5 of water at 15°. Its crystals are thin flat rhombic prisms, moderately deliquescent, and it may be purified by recrystallisation (unlike KNO_2). Potassium nitrite, m.p. 441°, forms minute short monoclinic prisms containing no water, not deliquescent when quite pure, and soluble in one-third the weight of water.

Barium nitrite is prepared by mixing hot, almost saturated solutions of equivalent amounts of sodium nitrite and barium chloride, filtering the sodium chloride in a hot-water funnel, and allowing the filtrate to crystallise: $2NaNO_2 + BaCl_2 \rightleftharpoons 2NaCl + Ba(NO_2)_2$. The salt is recrystallised and dried over sulphuric acid, when it forms $Ba(NO_2)_2,H_2O$ (Witt and Ludwig, *Ber.*, 1903, **36**, 4384).

Silver nitrite $AgNO_2$ is obtained as a yellowish-white, sparingly soluble (0·33 g. in 100 water at 15°) precipitate when alkali nitrite is added to silver nitrate solution. It is purified by recrystallisation from hot water. Nearly all other nitrites are soluble.

A dilute acid, even acetic, added to a nitrite solution, sets free **nitrous acid** HNO_2 but this decomposes, nitric oxide and nitrogen dioxide being liberated.

The solution has a pale blue colour, due to nitrous anhydride N_2O_3. The decomposition in fairly concentrated solutions is probably :

$$2HNO_2 \rightleftharpoons N_2O_3 + H_2O \rightleftharpoons NO + NO_2 + H_2O.$$

In dilute solutions it occurs according to the equation (Burdick and Freed, *J.A.C.S.*, 1921, **43**, 518 ; Taylor, Wignall and Cowley, *J.C.S.*, 1927, 1923) :

$$3HNO_2 \rightleftharpoons HNO_3 + 2NO + H_2O.$$

Pure dilute nitrous acid, obtained by precipitating a solution of barium nitrite with dilute sulphuric acid, is pale blue and slowly decomposes, especially on heating or shaking, with evolution of nitric oxide. The solution dissolves copper, silver and bismuth : $Cu + 4HNO_2 = Cu(NO_2)_2 + 2NO + 2H_2O$. It is rather a weak acid, $K_a = [H^{\cdot}]\,[NO_2']/[HNO_2]$ is 5×10^{-4} at 15°. The free acid can be titrated with alkali and alizarin red as indicator.

Nitrous acid and nitrites are *reducing* agents : $HNO_2 + O = HNO_3$; they reduce acid permanganate, dichromate and bromine water : $HNO_2 + H_2O + Br_2 = HNO_3 + 2HBr$, but not alkaline permanganate. They may be determined in solution by running into excess of warm acidified *N*/2 potassium permanganate and titrating the excess with standard oxalic acid :

$$2MnO_4' + 5NO_2' + 6H^{\cdot} = 2Mn^{\cdot\cdot} + 5NO_3' + 3H_2O.$$

Nitrous acid and nitrites sometimes act as *oxidising* agents :

$$2HNO_2 = 2NO + O + H_2O.$$

Iodine is liberated from acidified potassium iodide :

$$2I' + 2NO_2' + 4H^{\cdot} = I_2 + 2NO + 2H_2O,$$

indigo is bleached, stannous chloride is oxidised to stannic chloride :

$$2Sn^{\cdot\cdot} + 2NO_2' + 6H^{\cdot} = 2Sn^{\cdot\cdot\cdot\cdot} + N_2O + 3H_2O,$$

and ferrous to ferric salts :

$$2Fe^{\cdot\cdot} + 2NO_2' + 4H^{\cdot} = 2Fe^{\cdot\cdot\cdot} + 2NO + 2H_2O,$$

sulphur is precipitated from hydrogen sulphide, and sulphur dioxide is oxidised to sulphuric acid. In presence of atmospheric oxygen NO will reproduce nitrous acid, so that a small amount of nitrous acid acts as a carrier of oxygen.

The liberation of iodine from potassium iodide (blue colour with starch) is a test for nitrous acid or a nitrite in acid solution, but is not specific. Still more delicate are (i) the brown colour with a solution of metaphenylenediamine hydrochloride in hydrochloric acid, (ii) the intense pink colour with a mixture of solutions of sulphanilic acid and α-naphthylamine in acetic acid. These reactions are used to determine traces of nitrites in water.

Nitrites detonate violently when heated with thiosulphates or cyanides. A mixture of sulphur, potassium carbonate and nitre, or of nitre and potassium cyanide, detonates violently when heated. These mixtures sometimes cause surprises in qualitative analysis.

Nitrous acid may be formulated as H·O·N:O, *i.e.* H—O—N=O, the nitrite ion being [:O:N::O]′. The hydrogen atom in the acid or the radical R in the esters (*e.g.* $C_2H_5NO_2$, ethyl nitrite) is directly attached to oxygen : the esters on reduction yield alcohol and ammonia (with some hydroxylamine) : $RO{\cdot}N{=}O + 6H = ROH + NH_3 + H_2O$. In the nitro-compounds (*e.g.* $C_2H_5NO_2$, nitroethane), isomeric with nitrites and formed by the action of silver nitrite on alkyl iodides, the radical is directly attached to nitrogen, since on reduction they yield amines : $R{\cdot}NO_2 + 6H = R{\cdot}NH_2 + 2H_2O$. Silver and mercurous nitrites are pale yellow and may have the nitro-structure $Ag{\cdot}NO_2$.

Nitrosyl Compounds

Nitrous acid may be regarded as the hydroxide of the univalent radical *nitrosyl* —N=O, viz. HO - NO. Other nitrosyl compounds are the chloride NOCl, bromide NOBr, perchlorate $NOClO_4$, fluoborate $NOBF_4$ and hydrogen sulphate $(NO)HSO_4$, the last being nitrososulphuric acid or " chamber crystals " $SO_2(OH){\cdot}O{\cdot}NO$.

Nitrosyl chloride.—A mixture of 1 vol. of concentrated nitric acid and 4 vols. of concentrated hydrochloric acid, called *aqua regia* because it dissolves gold, on warming evolves an orange-yellow mixture of chlorine and nitrosyl chloride (Gay-Lussac, 1848) : $HNO_3 + 3HCl = NOCl + Cl_2 + 2H_2O$.

The gas is dried by calcium chloride and passed through concentrated sulphuric acid, when chlorine passes on but nitrosyl chloride is absorbed to form nitrososulphuric acid : $NOCl + H_2SO_4 = NO{\cdot}HSO_4 + HCl$. On warming with sodium chloride this evolves pure nitrosyl chloride (Tilden, *J.C.S.*, 1874, **27**, 630) : $NO{\cdot}HSO_4 + NaCl = NOCl + NaHSO_4$.

Nitric oxide and chlorine combine when mixed, the reaction being more rapid in presence of charcoal at 40°–50° : $2NO + Cl_2 = 2NOCl$. Nitrosyl chloride, as it is the chloride of nitrous acid, is formed by the action of phosphorus pentachloride on potassium nitrite :

$$PCl_5 + KNO_2 = NOCl + POCl_3 + KCl.$$

Nitrosyl chloride is an orange-yellow gas with a suffocating smell. It condenses in a freezing mixture to a ruby-red liquid, b.p. −5·5°, s. g. 1·4 at −12°, freezing to a lemon-yellow solid, m.p. −64·5°. The gas is readily decomposed by water and alkalis : $NOCl + H_2O = HNO_2 + HCl$; $NOCl + 2NaOH = NaNO_2 + NaCl + H_2O$. It has no action on gold or platinum but attacks mercury and most other metals : $2NOCl + 2Hg = 2NO + Hg_2Cl_2$. It is a stable gas but dissociates above 700° : $2NOCl \rightleftharpoons 2NO + Cl_2$. It forms compounds with many metal chlorides, *e.g.* $ZnCl_2$,NOCl and $FeCl_3$,NOCl (Sudborough, *J.C.S.*, 1891, **59**, 73, 270, 655) ; $MnCl_2$ and $FeCl_2$ form $MnCl_3(NO)$ and $FeCl_3(NO)$ (Gall and Megdehl, 1927).

Nitrosyl bromide NOBr is a blackish-brown liquid, b.p. −2°, m.p. −55·5°, formed by passing nitric oxide into bromine at −15°. At the ordinary temperature $NOBr_3$ is formed. **Nitrosyl fluoride** NOF is a colourless reactive gas, b.p.

$-59{\cdot}9°$, m.p. $-132{\cdot}5°$, formed by the reaction $NOCl + AgF = NOF + AgCl$ at 200°–250° (Ruff, etc., 1905–8).

The NOCl and NOBr molecules are bent, the $X - \hat{N} = O$ angle being 125°, and the N to O distance 1·12 A. The N to Cl (1·98 A.) and N to Br (2·14 A.) distances are much greater than the sum of the covalent radii (Ketelaar and Palmer, *J.A.C.S.*, 1937, **59**, 2629), indicating some contribution of an ionic structure $[:\ddot{X}:]^- [:N:::O:]^+$ by resonance.

Nitrosyl perchlorate $NOClO_4$ is formed in colourless crystals by passing $NO + NO_2$ into very concentrated perchloric acid (Hofmann and Zedwitz, 1909):

$$NO + NO_2 + 2HClO_4 = 2NOClO_4 + H_2O,$$

and **nitrosyl fluoborate** $NOBF_4$ similarly from HBF_4 (Wilke-Dörfurt and Balz, 1927).

Nitrosyl hydrogen sulphate $(NO)HSO_4$ or **nitrososulphuric acid** $SO_2(OH)\cdot O\cdot NO$ (" chamber crystals ") can be obtained in a number of ways. It was obtained by Clement and Desormes in 1806 by the interaction of oxides of nitrogen, sulphur dioxide, and a regulated amount of moisture:

$$3NO_2 + 2SO_2 + H_2O = 2SO_2(OH)\cdot O\cdot NO + NO,$$

and is supposed to be formed as an intermediate stage in the lead chamber process (p. 709). It is more conveniently made by passing the red vapours from arsenic trioxide and nitric acid (p. 576) into cooled concentrated sulphuric acid: $\boxed{NO + NO_2 \rightleftharpoons}\ N_2O_3 + 2H_2SO_4 \rightleftharpoons 2SO_2(OH)\cdot O\cdot NO + H_2O$, but is best prepared by passing sulphur dioxide into *cooled* fuming nitric acid and draining the white crystals on a porous tile in a desiccator (Weber, 1862): $SO_2 + HNO_3 = SO_2(OH)\cdot O\cdot NO$. Water decomposes it with effervescence, evolving red fumes. It dissolves in sulphuric acid containing not more than 35 p.c. of water, but more dilute acid decomposes it.

Nitrosyl hydrogen sulphate melts with decomposition at 73°, and forms white crystalline **nitrosyl disulphate** $(NO)_2S_2O_7$, or $O(NO\cdot O\cdot SO_2)_2$, which is more conveniently made by the action of liquid sulphur dioxide and nitrogen dioxide in a sealed tube (de la Provostaye, 1840; Jones, Price and Webb, *J.C.S.*, 1929, 312): $2SO_2 + 3NO_2 = (NO)_2S_2O_7 + NO$, or by the action of nitric oxide on sulphur trioxide at 200°: $3SO_3 + 2NO \rightleftharpoons (NO)_2S_2O_7 + SO_2$. **Nitrosyl hydrogen selenate** $(NO)HSeO_4$ and **fluosulphonate** $(NO)SO_3F$ are described (Hantzsch and Berger, 1930).

Nitrogen Dioxide

Nitrogen dioxide NO_2 was obtained by Priestley in 1777 (see Meldrum, *J.C.S.*, 1933, 905) by the action of *concentrated* nitric acid on copper:

$$Cu + 4HNO_3 = Cu(NO_3)_2 + 2NO_2 + 2H_2O$$

and by heating lead nitrate:

$$2Pb(NO_3)_2 = 2PbO + 4NO_2 + O_2.$$

Its formula was first correctly given by Gay-Lussac (1816) and by Dulong (1816), who distinguished it from N_2O_3. It is formed as a red gas by the combination of nitric oxide and oxygen: $2NO + O_2 = 2NO_2$. Below 140° it is partly associated to dinitrogen tetroxide N_2O_4: $2NO_2 \rightleftharpoons N_2O_4$, and the mixture is conveniently called *nitrogen peroxide* (Graham).

Bodenstein (1918–22) found that the reaction $2NO + O_2 = 2NO_2$ at 141° (when only NO_2 is formed) is termolecular: the first part is thus more rapid than the second, but it is incorrect to infer from this that N_2O_3 is first formed and then more slowly oxidised to N_2O_4.

The velocity of reaction *decreases* with rise of temperature; at −184° it is 100 times as fast as at 0°. This has been explained by supposing that N_2O_2 molecules are involved, which are dissociated on heating into NO.

According to Wourtzel (*Compt. rend.*, 1920, **170**, 109, 229) the velocity of oxidation is given by

$$-\mathrm{d}p_{NO}/\mathrm{d}t = kp_{NO}^2 p_{O_2}$$

where p is in mm. Hg and t in secs., and the velocity coefficient at different temperatures is:

t° C.	0°	25·2°	85·5°	100°	150°
10^4k	10·63	8·73	5·69	4·8	3·35

From this, the fractions of NO oxidised at 25·2° with the low initial pressures $p_{NO} = 6{\cdot}4$ mm. and $p_{O_2} = 0{\cdot}5$ mm. are: in 50 sec. 10 p.c., in 8·5 mins. 50 p.c., in 64 mins. 90 p.c. (see Todd, *Phil. Mag.*, 1918, **35**, 281, 435).

Nitrogen dioxide is often prepared by the decomposition of lead nitrate by heat: $2Pb(NO_3)_2 = 2PbO + 4NO_2 + O_2$.

EXPT. 22.—Heat *dry* powdered lead nitrate in a hard glass tube or retort and pass the gas evolved through a U-tube containing calcium chloride and then through a glass worm cooled in a mixture of ice and salt. A yellow liquid collects in a tube cooled in ice and salt (in presence of moisture it is green: $2N_2O_4 + H_2O = N_2O_3$ (blue) $+ 2HNO_3$). A glowing chip over the collecting tube bursts into flame, showing that oxygen is evolved. Pour the N_2O_4 on crushed ice in a test-tube. A deep blue layer rich in N_2O_3 separates: $2N_2O_4 + 2H_2O \rightleftharpoons 2HNO_2 + 2HNO_3 \rightleftharpoons N_2O_3 + 2HNO_3 + H_2O$ (Fritzsche, 1840).

A more convenient method is the action of nitric acid and phosphorus pentoxide on a mixture of nitrous anhydride and nitrogen dioxide obtained by distilling arsenious oxide with a mixture of concentrated nitric acid and half its weight of concentrated sulphuric acid (Ramsay and Cundall, *J.C.S.*, 1890, **57**, 590; 1891, **59**, 1076): $N_2O_3 + 2HNO_3 \rightleftharpoons 2N_2O_4 + H_2O$.

EXPT. 23.—Cool the blue liquid obtained in Expt. 21 in a freezing mixture, add excess of P_2O_5 and fuming nitric acid drop by drop until the colour changes to yellow. Distil and collect as before.

The best method of preparation is to heat nitrososulphuric acid ("chamber crystals") with dry potassium nitrate (Girard and Pabst, 1878; Park and Partington, *J.C.S.*, 1924, **125**, 72): $SO_2(OH)\cdot O\cdot NO + KNO_3 = N_2O_4 + KHSO_4$.

EXPT. 24.—Pass sulphur dioxide *slowly* into *well-cooled* fuming nitric acid in a retort until the liquid becomes pasty (nitrososulphuric acid). Add the calculated amount of dry powdered potassium nitrate, stir well, stopper the retort, heat gently and collect as above.

Nitrogen peroxide in a *good* freezing mixture (it supercools strongly) solidifies to pale yellow, nearly colourless, crystals melting at $-9{\cdot}04°$ to a honey-yellow liquid, s. g. 1·49 at 0°. The solid is probably almost entirely N_2O_4, which appears to be colourless. The liquid at the m.p. already contains some NO_2, which is strongly coloured. On warming the colour deepens; at 10° it is yellow, at 15° orange, and at 21·9° it is reddish-brown and the liquid boils giving a red vapour (Bousfield, *J.C.S.*, 1919, **115**, 45). The colour of the vapour darkens on further heating, as may be seen by comparing two bulbs containing it, one at the ordinary temperature; at 40° it is almost black.

The colour change accompanies a decrease in density (reduced to S.T.P.) up to 140°, when it corresponds with NO_2: $N_2O_4 \rightleftharpoons 2NO_2$. The figures below (Deville and Troost, 1867) are for 1 atm. pressure:

Temperature	Density (O = 16)	Dissociation p.c.
21·9° (b.p.)	39·81	15·7
26·7	38·4	20·1
60·2	30·2	52·8
100·1	24·4	89·3
135·0	23·2	99·1
140·0	22·91	100·0

The densities D referred to air = 1 are given by Gibbs's equation (from which the density at the b.p. in the table was calculated):

$$\log \frac{1{\cdot}589(D-1{\cdot}589)}{(3{\cdot}178-D)^2} = \frac{3118{\cdot}6}{t°\text{ C.}+273} + \log p_{mm} - 12{\cdot}451.$$

Above 140° the density decreases and the gas becomes paler, owing to the dissociation $2NO_2 \rightleftharpoons 2NO + O_2$, which is complete at 620° (Richardson, *J.C.S.*, 1887, **51**, 397). Recombination occurs on cooling:

$$N_2O_4 \text{ solid} \underset{-9{\cdot}04°}{\rightleftharpoons} N_2O_4 \text{ liq.} \underset{21{\cdot}9°}{\rightleftharpoons} N_2O_4 \text{ (vap.)} \underset{140°}{\rightleftharpoons} 2NO_2 \underset{620°}{\rightleftharpoons} 2NO + O_2.$$

The composition of nitrogen dioxide is found by passing it over copper heated to *bright* redness (otherwise NO is formed): $4Cu + 2NO_2 = 4CuO + N_2$.

Nitrogen peroxide vapour does not readily support the combustion of a taper, but strongly burning phosphorus and carbon burn in it. Solutions in liquid hydrocarbons are dangerously explosive. Potassium inflames in the gas and heated sodium burns in it. The gas and liquid attack mercury; tin is oxidised by the gas to dioxide. Finely divided copper reacts at room temperature to form cuprous oxide, which then adsorbs nitrogen dioxide; the so-called "nitro-copper" formed is not a definite compound (Park and Partington, *J.C.S.*, 1924, **125**, 72, 663): $2Cu + NO_2 = Cu_2O + NO$.

Carbon monoxide is oxidised at the ordinary temperature to carbon dioxide, and hydrogen sulphide deposits sulphur :

$$NO_2 + CO = NO + CO_2\,; \quad NO_2 + H_2S = NO + H_2O + S.$$

A mixture of nitrogen dioxide and hydrogen is reduced to ammonia when passed over heated platinum : $2NO_2 + 7H_2 = 2NH_3 + 4H_2O$.

On carefully adding cold water to liquid nitrogen peroxide cooled in a freezing mixture, or pouring the liquid on ice, a deep blue liquid rich in nitrogen trioxide separates : $2N_2O_4 + H_2O \rightleftharpoons N_2O_3 + 2HNO_3$.

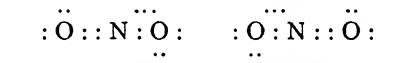
Nitrogen dioxide is absorbed by concentrated sulphuric acid to form nitroso-sulphuric acid and nitric acid, and since these decompose each other, a state of equilibrium is attained : $N_2O_4 + H_2SO_4 \rightleftharpoons SO_2(OH)\cdot O\cdot NO + HNO_3$. The gas is absorbed by alkalis with formation of nitrite and nitrate :

$$2KOH + N_2O_4 = KNO_2 + KNO_3 + H_2O.$$

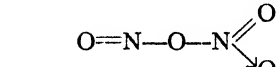
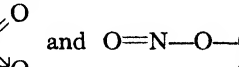
Baryta becomes incandescent at 200°. Quicklime and oxides of zinc, aluminium, and lead absorb the gas on heating, but free nitrogen and nitric oxide are liberated in the case of quicklime (Oswald, 1914 ; Partington and Williams, *J.C.S.*, 1924, **125**, 947) :

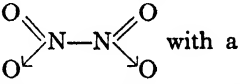
$$2CaO + 4NO_2 = Ca(NO_3)_2 + Ca(NO_2)_2$$
$$Ca(NO_2)_2 + 2NO_2 = Ca(NO_3)_2 + 2NO$$
$$Ca(NO_2)_2 + 2NO = Ca(NO_3)_2 + N_2.$$

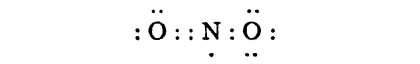
The structures of NO_2 and N_2O_4 are uncertain. NO_2, which contains an odd electron and is paramagnetic, may be a resonance hybrid with a three electron bond (Pauling, *J.A.C.S.*, 1931, **53**, 3225) :



The molecule is probably bent. N_2O_4 is diamagnetic and although the formulae

 and  have been suggested for it

(Divers, 1885, 1904), it appears to be  with a link between the nitrogens (Hendricks, 1931 ; Giauque and Kemp, *J. Chem. Phys.*, 1938, **6**, 40), so that the odd electron in NO_2 may be localised on the nitrogen :



Higher oxygen compounds of nitrogen.—Hautefeuille and Chappuis, and Berthelot (1881–2), by the action of a silent discharge on a mixture of nitrogen or NO_2 and oxygen, obtained a higher oxide of nitrogen which they supposed was ***nitrogen hexoxide*** N_2O_6. Later claims to have isolated solid N_2O_6 or NO_3 have not been substantiated (Klemenc and Neumann, 1937).

Raschig (1904–7) found that a mixture of hydrogen peroxide and acidified sodium nitrite solution liberates bromine from potassium bromide, which neither

does separately, and he supposed that *pernitric acid* HNO_4 was formed. D'Ans and Friederich (1911) thought this was formed by dissolving N_2O_5 in anhydrous H_2O_2: $N_2O_5 + H_2O_2 = HNO_4 + HNO_3$. According to Gleu (1929, 1935; *Ann. Rep. C.S.*, 1935, 156), in acidified nitrite solution containing hydrogen peroxide the ratio of active oxygen to *nitrite* radical, as determined in a special way, is 1.1, hence the oxidising substance is supposed to be **pernitrous acid** O=N—O—OH, isomeric with nitric acid.

Hyponitrous Acid

By reducing potassium nitrate solution with sodium amalgam, neutralising with acetic acid, and adding silver nitrate, Divers (1871) obtained a yellow precipitate of silver hyponitrite $Ag_2N_2O_2$.

Sodium hyponitrite is best prepared by reducing concentrated sodium nitrite solution with sodium amalgam (Divers, *J.C.S.*, 1899, **75**, 87, 95; Partington and Shah, *ibid.*, 1931, 2071).

To 25 g. of pure $NaNO_2$ dissolved in 75 c.c. of water, an amalgam of 25 g. of sodium in 140 c.c. of mercury is slowly added, the flask being cooled by water. The contents are transferred to a separating funnel and shaken for an hour, the mercury run off, and the solution filtered through asbestos. It is then left in a vacuum desiccator over concentrated sulphuric acid, which absorbs ammonia also formed. Granular crystals of $Na_2N_2O_2,5H_2O$ slowly separate. They are triturated with alcohol, and washed with alcohol and ether, when they form a white powder (s. g. 2·47) of anhydrous $Na_2N_2O_2$, which is dried in a desiccator and is fairly stable in air.

Hyponitrous acid is formed in small quantities by the action of nitrous acid on hydroxylamine (Wislicenus, 1893):

$$HO-N\boxed{H_2+O}=N\cdot OH = HO\cdot N = N\cdot OH + H_2O.$$

EXPT. 25.—To a solution of hydroxylamine sulphate add sodium nitrite solution, heat rapidly to 60°, and add silver nitrate solution. A *canary yellow* precipitate of silver hyponitrite is formed. (If the conditions are not correct, a yellowish-white precipitate of silver nitrite is obtained.)

Sodium hyponitrite is formed in poor yield by warming sodium hydroxylamine sulphonate with sodium hydroxide:

$$2HO\cdot NH\cdot SO_3Na + 4NaOH = Na_2N_2O_2 + 2Na_2SO_3 + 4H_2O.$$

The products formed on passing nitric oxide into a solution of sodium in liquid ammonia, or into the sodium compound of pyridine suspended in benzene: $2NO + 2Na = Na_2N_2O_2$, may not be true hyponitrites (Zintl and Harder, 1933).

On adding silver hyponitrite to an ether solution of hydrogen chloride in absence of moisture, and evaporating the filtrate in vacuum, leaflets of free **hyponitrous acid** separate, which explode feebly when dry, so that they cannot be analysed. The solution decomposes with evolution of nitrous oxide:

$$H_2N_2O_2 = N_2O + H_2O$$

(Hantzsch and Kaufmann, 1896; Partington and Shah, *J.C.S.*, 1932, 2589).

Hyponitrites are oxidised by acid permanganate to nitric acid :

$$5N_2O_2'' + 8MnO_4' + 24H^{\cdot} = 10NO_3' + 8Mn^{\cdot\cdot} + 12H_2O.$$

With alkaline permanganate a nitrite is formed. They are very stable towards reducing agents.

The doubled formula $H_2N_2O_2$ for hyponitrous acid is required by the following experimental evidence :

1. The acid and normal salts $Ba(HN_2O_2)_2$ and BaN_2O_2 are described.
2. The lowering of freezing point of the solution of the acid corresponds with $H_2N_2O_2$.
3. Esters, *e.g.* ethyl hyponitrite $Et_2N_2O_2$ (prepared by the action of ethyl iodide on silver hyponitrite), have molecular weights corresponding with the doubled formulae (Zorn, 1878 ; Partington and Shah, *J.C.S.*, 1932, 2593).
4. The esters have very small dipole moments in solution (Hunter and Partington, *J.C.S.*, 1933, 309), which agrees with the *anti*-configuration suggested by Hantzsch :

$$\begin{array}{l} HO—N \\ \quad\quad\| \\ \quad\quad N—OH \end{array}$$

On heating, the salts and esters of hyponitrous acid decompose (Partington and Shah, *J.C.S.*, 1932, 2589) :

$$3Na_2N_2O_2 = 2NaNO_2 + 2Na_2O + 2N_2$$
$$2CaN_2O_2 = 2CaO + 2NO + N_2$$
$$5CaN_2O_2 = Ca(NO_3)_2 + 4CaO + 4N_2$$
$$(CH_3CH_2)_2N_2O_2 = CH_3CH_2OH + CH_3CHO + N_2.$$

Nitramide $NO_2{\cdot}NH_2$ is the amide of nitric acid $NO_2{\cdot}OH$ and isomeric with hyponitrous acid. It is formed by the nitration of potassium imidosulphonate (p. 589) under special conditions, and subsequent hydrolysis :

$$\begin{array}{l} NH(SO_3K)_2 \rightarrow NO_2{\cdot}N \\ \quad\quad\quad\quad\quad\quad\quad\quad 2H \end{array} \left| \begin{array}{l} (SO_3H)_2 \rightarrow NO_2{\cdot}NH_2 + 2H_2SO_4 \\ \quad\quad\quad\quad\quad\quad\quad\quad OH \end{array} \right.$$

but a better method of preparation (Thiele and Lachmann, 1895–7) is to make potassium nitrocarbamate by the action of alcoholic potash on nitrourethane (urethane $EtO{\cdot}CO{\cdot}NH_2$ is the ethyl ester of carbamic acid $HO{\cdot}CO{\cdot}NH_2$) :

$$CO\begin{array}{l}\diagup NH{\cdot}NO_2 \\ \diagdown OEt\end{array} + 2KOH = CO\begin{array}{l}\diagup NK{\cdot}NO_2 \\ \diagdown OK\end{array} + H_2O + EtOH$$

and decompose this with sulphuric acid and crushed ice :

$$CO\begin{array}{l}\diagup NK{\cdot}NO_2 \\ \diagdown OK\end{array} + H_2SO_4 = CO\begin{array}{l}\diagup NH{\cdot}NO_2 \\ \diagdown OH\end{array} + K_2SO_4$$

$$CO\begin{array}{l}\diagup NH{\cdot}NO_2 \\ \diagdown OH\end{array} = CO_2 + NH_2{\cdot}NO_2.$$

The nitramide is extracted with ether and crystallises on evaporation (Hunter and Partington, *J.C.S.*, 1933, 309; Marlies and La Mer, *J.A.C.S.*, 1935, **57**, 2008). It forms white prismatic crystals, m.p. 72°, more stable than hyponitrous acid but readily decomposing with evolution of nitrous oxide: $NH_2{\cdot}NO_2 = N_2O + H_2O$. The solution is acid. Thiele and Lachmann also represented it as the imide of nitric acid $NH{=}NO{\cdot}OH$; Hantzsch's formulation as the *cis-* (or *syn-*) configuration corresponding with hyponitrous acid has been abandoned.

Nitrosamine $NO{\cdot}NH_4$ is said to be formed by grinding finely powdered solid N_2O_3 and NH_3 at low temperatures (Schwarz and Giese, 1934):

$$N_2O_3 + 2NH_3 = NO{\cdot}NH_2 + NH_4NO_2,$$

but is very unstable.

Hydronitrous acid H_2NO_2 is known as a yellow sodium salt Na_2NO_2 formed by the action of sodium on sodium nitrite dissolved in liquid ammonia. It explodes violently in moist air (Maxted, *J.C.S.*, 1917, **111**, 1016).

Hyponitric acid $H_2N_2O_3$ is formed as the sodium salt $Na_2N_2O_3$, which is precipitated, on adding methyl nitrate to a solution of free hydroxylamine and sodium methoxide in methyl alcohol (Angeli, 1896):

$$NH_2OH + CH_3NO_3 = H_2N_2O_3 + CH_3OH$$
$$H_2N_2O_3 + 2CH_3ONa = Na_2N_2O_3 + 2CH_3OH.$$

On acidification, nitric oxide is evolved: $H_2N_2O_3 = H_2O + 2NO$. The structure is unknown, nitrohydroxylamine $NO_2{\cdot}NH(OH)$, and $HO{\cdot}O{\cdot}N{=}N{\cdot}OH$ being possible.

Nitrogen sulphides.—Nitrogen sulphide N_4S_4 (Gregory, 1835; Fordos and Gélis, 1850; Ruff and Geisel, 1904–5) forms orange-red rhombic crystals. It is obtained by the action of dry ammonia on a solution of sulphur chloride and chlorine in benzene: $16NH_3 + 6SCl_2 = N_4S_4 + 2S + 12NH_4Cl$, or the action of ammonia on a solution of thionyl chloride in benzene, or by the action of sulphur on liquid ammonia: $10S + 4NH_3 \rightleftharpoons N_4S_4 + 6H_2S$. It melts at 178°, explodes on percussion, and is decomposed by cold water. It combines with chlorine to form a tetrachloride $N_4S_4Cl_4$ and reacts with S_2Cl_2 to form **thiotrithiazyl chloride** N_3S_4Cl, which is converted by nitric acid into a crystalline nitrate $N_3S_4{\cdot}NO_3$. The molecular weight of nitrogen sulphide in solution corresponds with the formula N_4S_4 but its structure is not certainly known (Arnold, Hugill and Hutson, *J.C.S.*, 1936, 1645). A blue modification is obtained by sublimation over silver gauze. **Nitrogen pentasulphide** N_2S_5 is a deep red liquid, m.p. 10°–11°, formed when N_4S_4 is heated in a sealed tube with carbon disulphide at 100°. It decomposes on heating.

Sulphonic acids of hydroxylamine.—The following compounds are sulphonic acid derivatives of hydroxylamine in which H is substituted by $-SO_2{\cdot}OH$:

Hydroxylamine
$HO{\cdot}NH_2$

$HO{\cdot}NH(SO_3H)$	$HO{\cdot}N(SO_3H)_2$	$HSO_3O{\cdot}N(SO_3H)_2$
. monosulphonic acid	**H. disulphonic acid**	**H. trisulphonic acid**
$SO_3H{\cdot}O{\cdot}NH_2$	$SO_3H{\cdot}O{\cdot}NH(SO_3H)$	
H. *iso*-monosulphonic acid	**H. *iso*-disulphonic acid**	

Hydroxylamine mono- and disulphonates are formed by the action of nitrites on bisulphites, as already described (p. 553).

By the action of KNO_2 on $KHSO_3$ in solution the disulphonate is formed :

$$KNO_2 + 3KHSO_3 = HO{\cdot}N(SO_3K)_2 + K_2SO_3 + H_2O,$$

and on adding lead dioxide to the solution the potassium salt of **hydroxylamine trisulphonic acid** is formed (Fremy, 1845 ; Haga, 1904) :

$$HO{\cdot}N(SO_3K)_2 + K_2SO_3 + PbO_2 = (KSO_3)O{\cdot}N(SO_3K)_2 + PbO + KOH.$$

With very dilute acid this loses one SO_3K, giving a salt of **hydroxylamine** *iso*-**disulphonic acid** $KSO_3{\cdot}O{\cdot}NH{\cdot}SO_3K$ (Raschig, Haga, 1906). **Hydroxylamine** *iso*-**monosulphonic acid,** which is the amide of Caro's acid (p. 719) and has oxidising properties, liberating iodine from potassium iodide, is obtained by the action of chlorosulphonic acid on hydroxylamine salts (Sommer, 1914) :

$$NH_2OH + ClHSO_3 = HCl + NH_2{\cdot}O{\cdot}SO_3H.$$

By oxidising a warm solution of potassium hydroxylamine disulphonate with lead dioxide a bluish-violet solution of **potassium nitrosodisulphonate** $ON(SO_3K)_2$ is formed : $2HO{\cdot}N(SO_3K)_2 + PbO_2 = 2ON(SO_3K)_2 + H_2O + PbO$. This deposits in golden yellow needles (Fremy, 1845). The blue solution is paramagnetic and probably contains the free radical with an odd electron :

$$KSO_3 : \underset{\cdot}{\overset{:O:}{\overset{\cdot\cdot}{N}}} : SO_3K,$$

but the yellow solid is diamagnetic and hence is probably dimeric $[ON(SO_3K)_2]_2$ (Asmussen, 1933).

By the action of sulphur dioxide on nitrososulphuric acid (chamber crystals) a very unstable purple liquid is formed which Raschig (*J.S.C.I.*, 1911, **30**, 166) regarded as **nitrosisulphonic acid** H_2SNO_5 or $O{=}N\begin{cases}SO_3H\\OH\end{cases}$, and he supposed it to play a part in the lead chamber reactions (p. 709). A violet-red colour formed on passing nitric oxide into a solution of ferrous sulphate in concentrated sulphuric acid he supposed to be due to the ferrous salt $FeSNO_5$. Manchot (1910), however, formulated this and similar red compounds formed with copper and mercury salts as nitroso-compounds $[Fe(NO)]SO_4$, and Hantzsch (1930) formulated the purple acid as a hydronitroso-salt $[NOH]'[HSO_4]'$ formed by reduction of nitrososulphuric acid $[NO]'[HSO_4]'$; this is supported by the Raman spectrum (Angus and Leckie, 1935). The purple liquid formed from dry NO and HCl at liquid air temperature may be $[NOH]'Cl'$ (Rodebush and Yntema, 1923).

Sulphonic acids of ammonia.—By substituting hydrogen in ammonia NH_3 by the sulphonic group $—SO_2{\cdot}OH$ three derivatives are formed :

$NH_2{\cdot}SO_2H$	$NH(SO_2H)_2$	$N(SO_2H)_3$
amidosulphonic acid	**imidosulphonic acid**	**nitrilosulphonic acid**

Crystals of **potassium nitrilosulphonate** are formed by the reaction between concentrated solutions of potassium disulphite and nitrite (Fremy, 1845) :

$$2K_2S_2O_5 + KNO_2 = N(SO_3K)_3 + K_2SO_3.$$

When boiled for a short time with water it forms **potassium imidosulphonate** (Raschig, 1887), from which nitramide can be prepared (p. 586) :

$$N(SO_3K)_3 + H_2O = NH(SO_3K)_2 + KHSO_4.$$

On boiling the imidosulphonate with water and chalk it hydrolyses to **amidosulphonic acid :**

$$NH(SO_3K)_2 + H_2O = NH_2SO_3H + KHSO_4.$$

Amidosulphonic acid (now usually called **sulphamic acid**) is more easily prepared by the action of sulphur dioxide on hydroxylamine (Raschig, 1887; Sisler and Audrieth, *J.A.C.S.*, 1939, **61**, 3389) :

$$NH_2OH + SO_2 = NH_2SO_3H,$$

and technically by heating urea with excess of 100 p.c. sulphuric acid (Baumgarten, 1936) :

$$CO(NH_2)_2 + 2H_2SO_4 = NH_2SO_3H + CO_2 + NH_4HSO_4.$$

With equimolecular proportions ammonium imidosulphonate is also formed by the reaction :

$$NH_2SO_3(NH_4) + NH_2SO_3H = NH(SO_3NH_4)_2.$$

Sulphamic acid is a white crystalline solid soluble in water and is a strong acid. It is used for fireproofing. The solution slowly hydrolyses :

$$NH_2SO_3H + H_2O = NH_3 + H_2SO_4 = NH_4HSO_4.$$

CHAPTER XX

PHOSPHORUS

BRAND, of Hamburg, by distilling evaporated urine obtained phosphorus (Greek *phos* light, *phero* I bear) in 1674–5; the phosphate in urine on heating forms sodium metaphosphate and this is reduced on strong heating with carbon (from charred organic matter): $4NaPO_3 + 5C = Na_4P_2O_7 + 5CO + 2P$. Brand made known his process to Krafft, who showed phosphorus at the Court of Charles II in 1677. There it was seen by Boyle, who was told by Krafft that it was obtained from a human source. Boyle (who called it *noctiluca*) rediscovered it by distilling evaporated urine with sand, and published the preparation in 1680. Kunckel in 1676 had independently rediscovered phosphorus (Partington, *Science Progress*, 1936, **30**, 402). Gahn about 1770 discovered calcium phosphate in bones, and Scheele prepared phosphorus from bone-ash. The process formerly used on the large scale (see below) for the preparation from bone-ash was devised by Scheele in 1777.

Phosphorus always occurs combined, the average percentage in the lithosphere being 0·157 and in ordinary soil 0·1 p.c. The primary minerals are probably *apatite* $3Ca_3(PO_4)_2,CaF_2$ and *chlorapatite* $3Ca_3(PO_4)_2,3CaCl_2$, which are hard and practically insoluble in dilute acids (see p. 376). From them, secondary deposits of *calcium phosphate* $Ca_3(PO_4)_2$ have been formed by weathering, although some consist of fossil bones. Phosphorus also occurs in meteorites.

The " soft phosphates ", *e.g. coprolites* (calcium phosphate of fossil excreta), and *Charleston phosphate* (27 p.c. P_2O_5) from river beds in South Carolina, are easily decomposed by sulphuric acid. " Hard " varieties are the Spanish minerals *estramadurite* (33 p.c. P_2O_5) and *sombrerite* (35 p.c. P_2O_5). *Redonda phosphate* (35–40 p.c. P_2O_5), a cheap and rich ore from the West Indies, is aluminium phosphate $AlPO_4$. *Wavellite* is basic aluminium phosphate $4AlPO_4,2Al(OH)_3,9H_2O$, and *vivianite* is ferrous phosphate $Fe_3(PO_4)_2,8H_2O$. The richest phosphate deposits are in North Africa and Florida.

Phosphorus compounds occur in vegetable and animal tissues, especially in seeds in which is concentrated in the germ (cereal grains, except rice, contain 0·4 p.c. of P). Yolk of eggs, nerves and brain, and bone-marrow contain fatty esters of phosphoric acid (*lecithins* or *glycero-phosphates*).

In order to repair tissue waste and provide phosphates for bones, phosphorus compounds are essential in foods. Plants take them from the soil as calcium phosphate, and bone-meal and calcium superphosphate (p. 376) are used as fertilisers.

Fresh bones contain about 58 p.c. (ivory 67 p.c.) of calcium phosphate with some calcium carbonate, fats, and organic matter containing nitrogen. Charred bones (animal charcoal) are used in decolorising sugar syrup. When no longer active they are burnt to *bone-ash* containing about 80 p.c. of calcium phosphate, with calcium carbonate and a little fluoride.

Phosphorus.is obtained by reducing phosphoric acid or a metal phosphate. Since the oxide P_2O_5 is stable and strongly exothermic : $2P + \frac{5}{2}O_2 = P_2O_5 + 360$ k. cal., an energetic reducing agent or a high temperature is required, and silica is usually added to form a silicate with the metal. On the small scale aluminium may be used with sodium metaphosphate and silica : $6NaPO_3 + 3SiO_2 + 10Al = 3Na_2SiO_3 + 5Al_2O_3 + 6P$, and on the large scale calcium phosphate, carbon and silica in the electric furnace.

EXPT. 1.—Mix 1 g. of powdered sodium metaphosphate, 0·5 g. of aluminium powder and 3 g. of fine white sand, all being dry. Heat strongly in a hard glass tube in a current of dry hydrogen. Phosphorus distils and condenses in the cool part of the tube (Frank, *J.S.C.I.*, 1898, **17**, 612).

In the old process for making phosphorus, bone-ash was decomposed by hot 60 p.c. sulphuric acid to form insoluble calcium sulphate and phosphoric acid. The phosphoric acid was filtered, evaporated, mixed with powdered coke and distilled in fireclay retorts at a bright-red heat (Readman, *J.S.C.I.*, 1890, **9**, 163, 473) :

$$Ca_3(PO_4)_2 + 3H_2SO_4 = 3CaSO_4 + 2H_3PO_4$$
$$H_3PO_4 = H_2O + HPO_3$$
$$4HPO_3 + 12C = 2H_2 + 12CO + P_4.$$

Phosphorus is now made by the direct reduction of a phosphate by carbon in presence of silica (Wöhler, 1829) at a high temperature in the electric furnace (Readman, Parker and Robinson process, 1888 ; Readman, *J.S.C.I.*, 1891, **10**, 445). This method can be used with " hard " phosphates, since the mineral is not treated with acid.

A mixture of phosphate, sand (or crushed quartz) and coke is fed into a closed electric furnace provided with an outlet above for gas and phosphorus vapour, a slag hole below, and an adjustable carbon electrode between which and the carbon base an electric arc is struck (Fig. 251). The large 12,000 k.w. modern furnaces are 20 m. high, and about 85–90 p.c. of the phosphorus is recovered with a power expenditure of 18–20 k.w.h. per kg. of P.

The phosphate is decomposed by silica at 1150° : $Ca_3(PO_4)_2 + 3SiO_2 = 3CaSiO_3 + P_2O_5$. The calcium silicate forms a molten slag. The phosphorus pentoxide vapour is reduced by carbon at about 1500°, forming carbon monoxide and phosphorus vapour : $P_2O_5 + 5C = 2P + 5CO$. The cooled gas is passed over water in condensers when crude phosphorus separates. The dark-coloured product is purified by melting under chromic acid solution, when some impurities oxidise and dissolve and others separate as a scum. The liquid phosphorus may be filtered by pressing

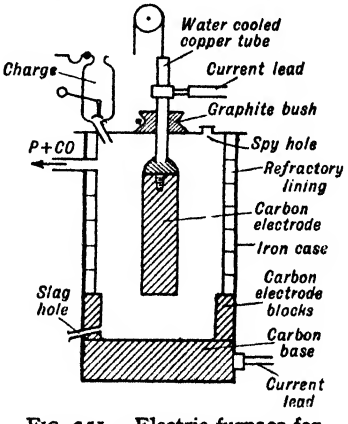


FIG. 251.—Electric furnace for phosphorus.

through chamois leather. The colourless phosphorus is cast into wedges (about 2 lb.) in tin moulds, or into sticks by running into glass tubes cooled in water and drawing out the stick at the other end.

Most of the phosphorus is used for matches, in making phosphor-bronze, as rat poison, and in the preparation of phosphorus trichloride, pentachloride and pentoxide.

Allotropic Forms of Phosphorus

Phosphorus exists in several allotropic forms, with two main divisions, *white* and *red*.

(1) **White phosphorus** : (*a*) *phosphorus I* (common), cubic crystals, s. g. 1·83, m.p. 44·1° (it supercools strongly), a non-conductor of electricity, soluble in carbon disulphide ; (*b*) *phosphorus II*, hexagonal, formed from P–I below – 69° or under 12,000 atm. pressure at 60° (Bridgman, *J.A.C.S.*, 1914, **36**, 1344), s. g. 2·699, probably a non-conductor of electricity and soluble in carbon disulphide.

(2) **Red phosphorus** : all varieties are insoluble in carbon disulphide : (*a*) *scarlet phosphorus*, amorphous, s. g. 1·876 ; (*b*) *phosphorus III* or *violet phosphorus* or *α-metallic phosphorus*, rhombohedral, s. g. 2·316 (or 2·34), m.p. 592·5°, a non-conductor of electricity ; (*c*) *phosphorus IV* or *black phosphorus* or *β-metallic phosphorus*, crystalline, s. g. 2·69, m.p. 587·5°, a fairly good conductor of electricity, ignites in air at about 400°. Ordinary " red phosphorus " (formerly, incorrectly, called " amorphous " phosphorus) is apparently a mixture of scarlet phosphorus and violet phosphorus.

White phosphorus is commonly a white translucent soft waxy solid which can be cut under water with a knife. On exposure to light it becomes yellow. Below 5·5° it is brittle and the crystalline structure is seen after etching with nitric acid. Large transparent crystals of the cubic system, usually rhombdodecahedra, with a play of colours like diamonds, are formed by slow sublimation in the dark in a vacuous tube kept cool at one end by a moist cloth (Herman, *J.S.C.I.*, 1888, **7**, 9).

White phosphorus melts at 44·1° and boils at 287°, the density of the colourless vapour corresponding with P_4 (Chapman, *J.C.S.*, 1899, **75**, 734). Above 700° dissociation occurs : $P_4 \rightleftharpoons 2P_2$ (1 p.c. at 800°, 33 p.c. at 1200° and 1 atm. and 66 p.c. at $\frac{1}{4}$ atm. pressure ; Stock, 1912). At very high temperatures dissociation into atoms occurs : $P_2 \rightleftharpoons 2P$.

White phosphorus is very sparingly soluble in water (1 in 300,000), but dissolves in benzene, turpentine, olive oil, sulphur chloride, phosphorus trichloride, and especially carbon disulphide (9 parts of P in 1 part of CS_2). From the elevation of boiling point of carbon disulphide Beckmann (1890) found the formula P_4, agreeing with that of the vapour, and Hertz (1890) found the same result from the depression of freezing point of benzene. On evaporation out of contact with air, the solution in carbon disulphide deposits crystals.

White phosphorus inflames spontaneously in chlorine, explodes violently in contact with liquid bromine and inflames in contact with solid iodine. It dissolves slowly in cold concentrated nitric acid to form phosphoric acid, and in hot alkali hydroxide solution with evolution of phosphine PH_3.

When exposed to the air at room temperature white phosphorus slowly oxidises with a greenish glow, forming fumes of a lower oxide and some ozone (p. 598). About 50° it takes fire in dry air, burning with a white flame to fumes of phosphorus pentoxide. Since it is easily inflamed by friction care should be used in drying with filter paper a piece cut under water. Phosphorus does not burn when heated in pure oxygen dried with phosphorus pentoxide (Baker, *Phil. Trans.*, 1888, **179**, 571). Finely divided white phosphorus inflames spontaneously in air, and melted white phosphorus burns under water in contact with oxygen.

EXPT. 2.—Pour a solution of phosphorus in carbon disulphide on a piece of blotting-paper supported on a tripod. The solvent rapidly evaporates and the finely divided phosphorus catches fire and burns with the formation of fumes of P_2O_5 (Lampadius, 1806). A solution in ether shows phosphorescence when poured on hot water or rubbed on the skin.

EXPT. 3.—Place a few bits of phosphorus in water in a test-tube supported in a beaker of water. Heat the water in the beaker and pass a current of oxygen through a tube into the water in the test-tube above the phosphorus. When the temperature reaches 60° the phosphorus takes fire and burns under water in contact with the oxygen, forming flakes of red phosphorus and a solution of phosphoric acid.

Sticks of white phosphorus under water in presence of air slowly acquire a white crust, which is ordinary phosphorus detached by unequal oxidation; according to Baudrimont (1865) it is not formed in water free from air. This crust slowly turns red and the colour spreads through the mass.

White phosphorus is very poisonous, the lethal dose being about 0·15 g. Workmen exposed to the vapour are liable to decay of the bones, especially of the jaw (" phossy-jaw "), and its use in the manufacture of matches has ceased.

The modern " strike anywhere " matches have heads containing phosphorus sulphide P_4S_3, oxidising agents such as potassium chlorate or manganese dioxide, glue or gum as a binder, and powdered glass to increase the friction. The heads of safety matches contain no phosphorus but are compounded of antimony sulphide and sulphur and oxidising agents such as potassium chlorate and red lead, whilst the strip on the box contains red phosphorus, powdered glass and a binder.

Red phosphorus was prepared by Schrötter in 1845 by heating white phosphorus for a few hours at 250° in a flask filled with nitrogen or carbon dioxide. The liquid deposits a red powder and finally solidifies to a purplish-red mass. The transformation begins at about 215°, is fairly rapid at 250°, and at higher temperatures it is reversible and is strongly exothermic: P (white) = P (red) +4·22 k. cal. Red phosphorus also remains when white phosphorus burns in air, or in oxygen under water, and was formerly thought to be a suboxide.

Brodie (1853) showed that the transformation is catalysed by a little iodine, and then occurs at 200°. The change occurs when a little iodine or selenium is added to a solution of white phosphorus in carbon disulphide, and when this

solution is exposed to strong light, red phosphorus (insoluble in carbon disulphide) deposits.

Red phosphorus is made by heating about a ton of white phosphorus in a large cast-iron pot with a cover, through which passes an upright iron tube. The pot is uniformly heated at 240°, the temperature being controlled by thermometers protected by iron tubes, since phosphorus attacks glass. A little phosphorus burns, absorbing oxygen from the air in the vessel. The hard solid in the pot is ground under water and boiled with caustic soda solution to remove unchanged white phosphorus. It is repeatedly washed with hot water and dried with steam. It usually contains about 0·5 p.c. of white phosphorus and some phosphoric acid.

Commercial red phosphorus is a violet-red powder, s. g. 2·1–2·2, without smell or taste and is not poisonous. It is a feeble conductor of electricity. It melts under pressure at 592·5° (Chapman, *J.C.S.*, 1899, **75**, 734), but on heating at atmospheric pressure is converted directly into vapour, which condenses to white phosphorus on cooling.

EXPT. 4.—Heat a little red phosphorus in a hard glass test-tube in a slow current of dry carbon dioxide passed through a tube in a rubber stopper also fitted with an outlet tube. White phosphorus condenses on the upper cool part of the test-tube.

Red phosphorus in general is much less reactive than white phosphorus. It does not glow in air but on exposure becomes moist from slow oxidation to phosphoric acid (Pedler, *J.C.S.*, 1890, **57**, 599). It does not ignite in air below 240°, does not burn in chlorine unless heated, burns quietly in contact with liquid bromine, and does not inflame in contact with solid iodine but combines without incandescence on heating. It is insoluble in carbon disulphide and in hot alkali hydroxide solution, but dissolves in concentrated nitric acid, rapidly on heating.

White phosphorus is metastable under all conditions and tends to pass into red, although the change is very slow at the ordinary temperature in the dark. If liquid white phosphorus is contained in one limb of a ∩-tube at 324° and solid red phosphorus in the other limb at 350°, distillation occurs to the hotter limb.

Ordinary red phosphorus was thought by Schrötter to be amorphous, but it really contains small rhombohedral crystals (Pedler, *J.C.S.*, 1890, **57**, 599; Retgers, 1893). The colour varies according to the temperature of preparation, from reddish-yellow through bright sealing-wax red (s. g. 2·15), to dark violet-red (s. g. 2·34) after long heating. The colour depends on the particle size and the extent of development of crystalline form. Yellow and scarlet forms are amorphous, and some kinds of commercial red phosphorus are mixtures of the scarlet amorphous and the violet crystalline forms.

Scarlet amorphous phosphorus is obtained as a fine powder by exposing a solution of white phosphorus in carbon disulphide or phosphorus tribromide to sunlight, when the yellow powder first deposited turns red (Pedler), or by boiling a 10 p.c. solution of white phosphorus in phosphorus tribromide for ten

hours (Schenck, *J.S.C.I.*, 1903, **22**, 1226). It is a fine scarlet powder, s. g. 1·876, more active than common red phosphorus, but oxidising only very slowly in air, and is not poisonous. It dissolves in alkali with evolution of phosphine and turns black. Prepared in this way it contains phosphorus tribromide; it may be obtained pure by heating phosphorus tribromide with mercury at 240° (Wolf, 1915): $2PBr_3 + 3Hg = 2P + 3HgBr_2$.

The *crystalline forms of red phosphorus* are called **Phosphorous-III** and **Phosphorous-IV**.

The common form is **Phosphorous-III** or **violet phosphorus** (also called *α-metallic phosphorus*), discovered by Hittorf in 1865. It is formed by heating ordinary red phosphorus in a sealed tube at 530°, the upper part of the tube being kept at 444°, when it sublimes in brilliant opaque rhombohedral crystals, isomorphous with As, Sb and Bi, s. g. 2·316 or 2·34, m.p. 592·5°. The crystals are also formed by dissolving white phosphorus in fused lead or bismuth in a sealed tube, allowing to crystallise, and dissolving out the metal in dilute nitric acid or electrolytically (Stock and Gomolka, *Ber.*, 1909, **42**, 4510). It does not oxidise in air and is a non-conductor of electricity. It is probably the same as the **violet phosphorus**, s. g. 2·35, m.p. 589·5, obtained by Bridgman (*J.A.C.S.*, 1916, **38**, 609) by heating white phosphorus with a trace of sodium under very high pressure.

Phosphorous-IV or **black phosphorus** or *β-metallic phosphorus*, discovered by Bridgman (*J.A.C.S.*, 1914, **36**, 1344; *Proc. Nat. Acad. Sci.*, 1935, **21**, 109; Hultgren, etc., *J. Chem. Phys.*, 1935, **3**, 351; Thomas and Gingrich, *ibid.*, 1938, **6**, 659), is crystalline, s. g. 2·69, m.p. 587·5°, and is formed irreversibly from white phosphorus at 200° under a pressure of 12,000 kg./sq. cm. It does not ignite at 400° in air and is a fairly good conductor of electricity.

A provisional *phase diagram* for phosphorus is shown in Fig. 252, but the actual relations are rather complicated (Smits and Bokhorst, *Z. phys. Chem.*, 1916, **91**, 249; Findlay, *Phase Rule*, 1938, 60). The curves and transition points are similar to those for the sulphur system (p. 53).

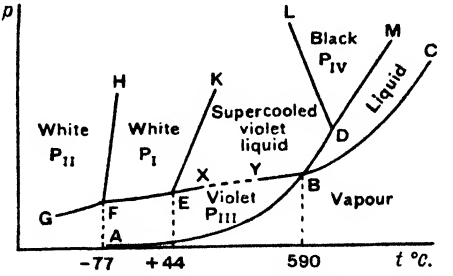


FIG. 252.—Phase diagram of phosphorus.

AB is the vapour pressure curve of solid violet phosphorus (P-III), lying below the curves of the metastable forms. *FE* is the curve of solid white phosphorus (P-I) and *EX* that of the liquid, probably continuous with the vapour pressure curve *BY* of liquid violet phosphorus. *BD* represents the equilibrium between violet phosphorus and liquid and the transition point *D* to black phosphorus (P-IV) is a triple point (P-III, P-IV, liquid). *DL* gives the variation of the transition temperature of violet to black with change of pressure. *C* is the critical point of liquid phosphorus, about 695° and 82 atm. The values of dT/dp along *FH* (P-II ⇌ P-I) and *EK* (P-I ⇌ liq.) are 0·012° and 0·029° per atm., respectively.

The glow of phosphorus.—The vapour pressure of white phosphorus at 20° is 0·027 mm. and the vapour oxidises spontaneously in air, emitting a faint green glow and white fumes. The glow is produced with mere traces of phosphorus vapour (5×10^{-5} p.c. in a gas in the absence of inhibitors), and is used as a test for free white phosphorus (*Mitscherlich's test*).

EXPT. 5.—A piece of white phosphorus is boiled in water in a flask connected with a Liebig's condenser. Phosphorus distils with the steam and a glow is seen in a dark room at the place where the vapour and steam condense in the tube.

EXPT. 6.—In Smithells' *cold flame* experiment, a few pieces of dry white phosphorus are placed in a dry bolt-head and covered with dry glass wool, the flask is heated on a water-bath, and a stream of dry carbon dioxide passed through (Fig. 253). The phosphorus vapour oxidises in the air and a green flame appears at the top of the exit tube. This is so cool that a finger may be held in it, and it will not kindle a match.

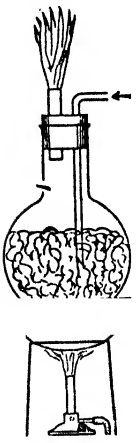


FIG. 253.—The cold flame experiment.

The **glow of phosphorus** (Thorpe, *Nature*, 1890, **41**, 523; Downey, *J.C.S.*, 1924, **125**, 347) was first investigated by Boyle (1680–82), who discovered most of its main features:

(i) Phosphorus glows only in presence of air.
(ii) An acid is formed which differs from phosphoric acid in giving little flashes of light on heating [phosphine from phosphorous acid].
(iii) The glow is produced by very small quantities of phosphorus (1 part in 500,000 parts of water).
(iv) The glow is produced by solutions of phosphorus in olive oil and some other oils, but oils of mace and aniseed prevent it.
(v) After long exposure to phosphorus, air acquires a strong odour [ozone] distinct from the visible fumes.

About the same time, Lemery, Slare and Hawksbee found that the glow is brighter at lower air pressures. Lampadius showed that it is extinguished in a Torricellian vacuum (the space in a barometer tube), so that a trace of oxygen is necessary. Fourcroy in 1788 found that phosphorus does not glow in ordinary moist oxygen at atmospheric pressure, but Bellani de Monza in 1813 showed that the glow appears if the oxygen pressure is reduced, an observation confirmed by Schweigger in 1824 and Graham in 1829.

According to Russell (*J.C.S.*, 1903, **83**, 1263), phosphorus glows very feebly at atmospheric pressure in oxygen dried by sulphuric acid, or even at higher pressures if the surface is very clean, lower oxides of phosphorus being produced. At pressures lower than 500 mm. at room temperature the glow in dry oxygen becomes much brighter and phosphorus pentoxide is formed. Ozone is not formed in dry oxygen. The main product of the glow in air at ordinary temperature is phosphorus dioxide P_2O_4 (not P_2O_3), with some P_2O_5 (Miller, *J.C.S.*, 1929, 1829).

According to Dixon and Baker (1889) phosphorus does not glow at any pressure in oxygen dried by phosphorus pentoxide. The glow appears in ordinary oxygen if this is mixed with an inert gas, and phosphorus glows in ozonised oxygen at atmospheric pressure. In oxygen at atmospheric pressure the glow appears at 27° and is very bright at 36°, when the phosphorus very easily inflames.

A stick of phosphorus is placed in the constricted part of a tube containing oxygen confined over mercury, the levelling tube being adjusted so that the gas is at atmospheric pressure (Fig. 254). No glow is seen in the dark. If the levelling tube is lowered so as to reduce the pressure, the phosphorus begins to glow. The following experiment is more convenient, as there is no danger of the phosphorus taking fire.

FIG. 254.—Effect of pressure on the glow of phosphorus.

EXPT. 7.—Heat a piece of phosphorus with olive oil in a flask on a water-bath. Cool the solution and pour it into a round litre flask fitted with a rubber stopper with two delivery tubes. Displace the air by dry oxygen. The glow ceases. Close one tube with rubber tubing and a clip and connect the other with an air-pump. Shake the liquid round the inside of the flask. On reducing the pressure of the oxygen the glow commences again suddenly at a certain reduced pressure.

Graham (1829) found that the glow is inhibited by the vapours of ether, naphtha, and turpentine. (The action of essential oils had been observed by Boyle.) One part of turpentine vapour in 4444 parts of air was sufficient. Later observers found that the vapours of many essential oils, camphor, naphthalene, carbon disulphide, and especially iodobenzene, inhibit the glow.

Schönbein (1848) related the glow to the formation of ozone, since (1) essential oils which destroy or dissolve ozone inhibit the luminosity, (2) at low temperatures no ozone is formed and phosphorus does not glow, (3) at 25° the glow is brightest and the production of ozone is a maximum. It is doubtful if ozone is directly formed by the glow reaction, and Downey reported that ozone is formed by the action of the ultra-violet light of the glow on oxygen, being formed when this light is passed into oxygen through a quartz or fluorite window; Busse (1927) and Fischbeck and Eich (*Ber.*, 1938, **71**, 520) could not confirm this.

An old theory that the glow was due to the oxidation of P_2O_3 first formed was disproved by Miller (*Proc. R.S. Edin.*, 1926, **46**, 76; *J.C.S.*, 1928, 1847; 1929, 1823, 1829), who showed that carefully purified P_2O_3, freed from white phosphorus by recrystallisation from CS_2, exposure to light, and sublimation, does not glow in air and also inhibits the glow of phosphorus.

The glow reaction occurs between phosphorus *vapour* and oxygen, since it is brighter at lower pressures, and an indifferent gas (N_2 or H_2) when passed over phosphorus glows when mixed with oxygen. In a stream of air the glow is detached from the solid phosphorus. There is also a lower limit of oxygen

pressure below which phosphorus does not glow. The glow seems to be the result of a chain reaction (p. 784), involving the production of lower oxides of phosphorus, taking place between P_4 and O_2 molecules. (Semenoff, *Chem. Reviews*, 1929, **6**, 347; *Kinetics of Chain Reactions*, Oxford, 1935; Rayleigh, *Proc. Roy. Soc.*, 1921, **99**, 372). A *tentative* scheme of reactions is:

$$\left.\begin{aligned} P_4 + O_2 &= 2PO + P_2 \\ P_2 + O_2 &= 2PO \end{aligned}\right\}$$ (PO bands are found in the glow spectrum).

$$PO + O_2 \begin{cases} \nearrow PO_3 \\ \searrow PO_2 + O \end{cases}$$ (an oxidising product, bleaching indigo, is formed).

$$2PO_2 = P_2O_4$$ (the chief product of slow oxidation).

$$O + O_2 = O_3$$ (ozone is a by-product of the glow reaction).

$$O + P_2O_4 = P_2O_5$$ (O_2 does not react with P_2O_4 below 25°).

Phosphorus Hydrides

Two well-defined phosphorus hydrides are known, the gaseous **phosphorus trihydride** PH_3 (*phosphine* or *phosphoretted hydrogen*) and the liquid **phosphorus dihydride** P_2H_4. Some ill-defined solid hydrides ($P_{12}H_6$, P_5H_2 and P_9H_2) are probably impure red phosphorus.

Phosphine PH_3 was discovered by Gengembre in 1783 by heating white phosphorus with alkali (see below). Traces are formed by heating white or red phosphorus in hydrogen (Retgers, 1894; Ipatiev and Nikolaiev, 1926) or by adding bits of white phosphorus to a mixture of zinc and dilute sulphuric acid evolving hydrogen, which then burns with a green flame (Brössler, 1881; this is a sensitive test for free white phosphorus). It is formed by the putrefaction of proteins (Gautier and Étard 1882) and the bacterial reduction of phosphates in the soil (Rudakov, 1927), and its spontaneous inflammability has been invoked to explain the *Will-o'-the-wisp* seen in marshes.

Phosphine is usually prepared by heating white phosphorus with concentrated sodium or potassium hydroxide solution, or a paste of slaked lime, when hydrolysis occurs and a hypophosphite is also formed:

$$P_4 + 3OH' = PH_3 + 3PO'$$
$$3PO' + 3H_2O = 3H_2PO_2',$$

or for the total reaction:

$$P_4 + 3NaOH + 3H_2O = 3NaH_2PO_2 + PH_3.$$

Some hypophosphite is decomposed, so that 60 p.c. of hydrogen may be present in the gas: $NaH_2PO_2 + 2NaOH = 2H_2 + Na_3PO_4$; baryta gives a purer gas. Hydrogen is also evolved by the direct reaction:

$$2P + 2NaOH + 2H_2O = 2NaH_2PO_2 + H_2.$$

Pure phosphine may be obtained by absorbing it from the gas in a solution of cuprous chloride in hydrochloric acid (when $CuCl,PH_3$ is formed), heating the solution, and drying the gas with KOH and P_2O_5 (Riban, 1879).

Expt. 8.—A few pieces of white phosphorus are placed in a flask (Fig. 255) containing 30–40 p.c. caustic soda solution. The air is displaced by coal gas to avoid explosion, and the flask heated to a fairly high temperature. Each bubble of phosphine which escapes from the delivery tube dipping into water ignites spontaneously with a bright flash, and a vortex-ring of white smoke (particles of metaphosphoric acid) rises in the air.

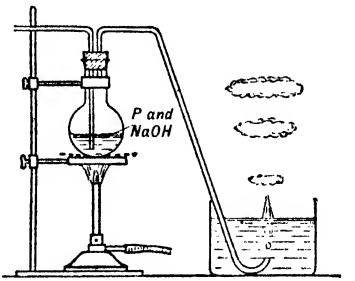


Fig. 255.—Preparation of phosphine.

A spontaneously inflammable gas is formed by the action of water on crude calcium phosphide :

$$Ca_3P_2 + 6H_2O = 3Ca(OH)_2 + 2PH_3.$$

Expt. 9.—A few pieces of calcium phosphide are dropped into a beaker of water and covered with an inverted funnel immersed in the water. The bubbles of gas inflame spontaneously in air.

A purer gas is formed by the action of dilute hydrochloric acid on calcium phosphide. The gas from *pure* calcium phosphide is not spontaneously inflammable (Moissan, 1899).

The spontaneous inflammability of ordinary phosphine is, as Le Verrier (1835) suspected and Thenard (1844) proved, due to a small amount of the vapour of the liquid hydride also formed :

$$6P + 4NaOH + 4H_2O = 4NaH_2PO_2 + P_2H_4.$$

Thenard showed that if the gas is passed through a tube immersed in a freezing mixture, the liquid hydride deposits and the gas is no longer spontaneously inflammable. The same result is obtained by passing the gas over recently ignited charcoal, which adsorbs the vapour of the dihydride, or by mixing the gas with a little ether vapour. The pure gas becomes spontaneously inflammable if mixed with a little vapour of fuming nitric acid.

Phosphine evolved on heating phosphorous acid (Davy, 1812) :

$$4H_3PO_3 = 3H_3PO_4 + PH_3$$

is not spontaneously inflammable but may contain 6 p.c. of hydrogen (Hofmann, *Ber.*, 1871, **4**, 200).

Pure phosphine is prepared (i) by dropping 30 p.c. potassium hydroxide solution on phosphonium iodide mixed with broken glass :

$$PH_4I + KOH = KI + H_2O + PH_3,$$

washing with hydrochloric acid (to decompose P_2H_4) and sodium hydroxide (to remove HI) and drying with P_2O_5 (Hofmann, *loc. cit.*), (ii) by the action of dilute sulphuric acid on aluminium phosphide (prepared by heating aluminium powder and red phosphorus) :

$$2AlP + 3H_2SO_4 = Al_2(SO_4)_3 + 2PH_3.$$

Phosphine is a colourless gas with a very unpleasant smell of rotten fish and is poisonous ; normal density 1·5307 g./lit., m.p. $-132{\cdot}5°$, b.p. $-87{\cdot}4°$. It is sparingly soluble in water (0·26 vols. in 1 of water at 17°), alcohol and ether ; a crystalline *hydrate* (PH_3,H_2O or PH_4OH ?) is formed by releasing the pressure on a mixture of the liquid and water. The gas is decomposed at 440° by a first order reaction largely on the surface of the vessel (Hinshelwood and Topley, *J.C.S.*, 1924, **125**, 393), and by electric sparks, 2 vols. depositing red phosphorus and giving 3 vols. of hydrogen : $2P_xH_y = 2xP + 3H_2$, $\therefore y = 3$ and the formula is P_xH_3. The density shows that the mol. wt. is 34, $\therefore$ the molecule contains $34 - 3 = 31$ parts of phosphorus, or 1 at. wt., hence $x = 1$ and the formula is PH_3. When passed over heated copper it forms copper phosphide and hydrogen.

Pure phosphine inflames in air at about 150° (when very dry it is said to inflame at room temperature). When burnt in a test-tube it deposits phosphorus (cf. H_2S, p. 695). A mixture of pure phosphine with air or oxygen explodes when the pressure is reduced (Labillardière, 1817). Mixtures with nitric and nitrous oxides explode when sparked : $PH_3 + 4N_2O = H_3PO_4 + 4N_2$. Phosphine ignites spontaneously in chlorine : $PH_3 + 4Cl_2 = PCl_5 + 3HCl$. It combines with many metallic chlorides. The pure gas is completely absorbed by a solution of bleaching powder. It precipitates phosphides or metals from solutions of many metallic salts (*e.g.* $CuSO_4$, $AgNO_3$) (Walker, *J.C.S.*, 1926, **128**, 1370). These phosphides are also formed by heating the solutions with white phosphorus, or the metals with phosphorus, or the phosphates with carbon in the electric furnace.

EXPT. 10.—Heat a few pieces of white phosphorus with a solution of copper sulphate. Black copper phosphide Cu_3P is formed :

$$3P + 3CuSO_4 + 6H_2O = Cu_3P + 2H_3PO_3 + 3H_2SO_4.$$

In the cold, metallic copper is deposited :

$$2P + 5CuSO_4 + 8H_2O = 5Cu + 2H_3PO_4 + 5H_2SO_4.$$

From silver nitrate solution, phosphine precipitates silver, a yellow intermediate compound being formed (cf. AsH_3, p. 623) :

$$PH_3 + 6AgNO_3 = Ag_3P,3AgNO_3 + 3HNO_3$$
$$Ag_3P,3AgNO_3 + 3H_2O = 6Ag + 3HNO_3 + H_3PO_3.$$

Phosphonium compounds.—Although phosphine is neutral it can act as a feeble base, forming **phosphonium salts** PH_4X analogous to ammonium salts NH_4X. A mixture of phosphine and dry hydrogen chloride does not react at atmospheric pressure, but if cooled to $-35°$ or compressed to 18 atm. at 15°, it deposits white cubic crystals of **phosphonium chloride** which dissociate again on warming or on reducing the pressure : $PH_3 + HCl \rightleftharpoons PH_4Cl$. **Phosphonium bromide** PH_4Br is more stable and is produced in cubic crystals when a mixture of PH_3 and HBr gas is led into a moderately cooled flask or phosphine is passed into cold saturated hydrobromic acid (Ogier, 1879). **Phosphonium iodide** PH_4I (Davy, 1812) is fairly stable and is formed in white tetragonal crystals on mixing PH_3 and HI gas at the ordinary temperature and pressure. It dissociates

at 30° but the crystals can be sublimed. It is most conveniently prepared by the following process (Baeyer, *Annalen*, 1870, **155**, 266).

EXPT. 11.—10 g. of white phosphorus are dissolved in an equal weight of carbon disulphide in a tubulated retort, from which the air has been removed by a current of dry carbon dioxide : 17 g. of iodine are then added and the carbon disulphide is distilled off completely on a water-bath in a current of CO_2. After cooling, the neck of the retort is connected with a wide glass tube and receiver

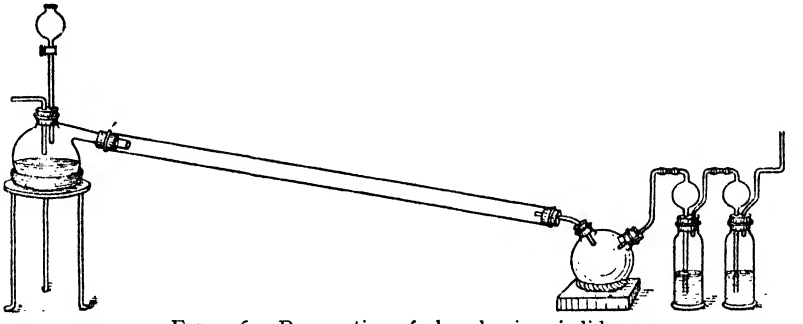


FIG. 256.—Preparation of phosphonium iodide.

and 8·5 c.c. of water are dropped gradually on to the phosphorus iodide (Fig. 256). The retort is then heated, at first gently, later more strongly to sublime the PH_4I into the tube. Two wash-bottles containing water are attached to the receiver, to absorb the hydriodic acid evolved : $2P + I_2 + 4H_2O = PH_4I + H_3PO_4 + HI$.

White deliquescent crystals of **phosphonium sulphate** $(PH_4)_2SO_4$(?) are said to be formed on passing PH_3 into strongly cooled concentrated sulphuric acid : water decomposes it into phosphine and sulphuric acid (Besson, 1889).

Phosphorus dihydride P_2H_4 is condensed as a colourless liquid from crude phosphine by passing through a tube cooled in a freezing mixture.

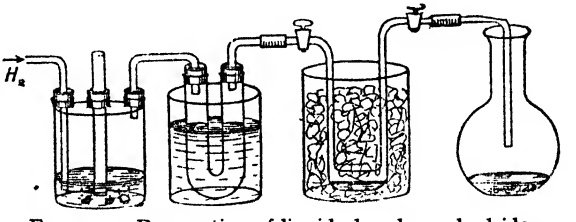


FIG. 257.—Preparation of liquid phosphorus hydride.

In the preparation of the liquid hydride pieces of calcium phosphide are dropped through a wide tube into water at 60° in a Woulfe's bottle (Fig. 257), the air being previously displaced by hydrogen. The gas is passed through a tube cooled in water to deposit moisture and the liquid condensed in a Hofmann tube cooled in a freezing mixture (Thenard, 1844 ; Gattermann and Hausknecht, *Ber.*, 1890, **23**, 1174).

The gas formed by the action of water on crude calcium phosphide, perhaps containing Ca_2P_2 (Ca=P·P=Ca), is fairly rich in P_2H_4 vapour :

$$Ca_2P_2 + 4H_2O = 2Ca(OH)_2 + P_2H_4.$$

The calcium phosphide is a reddish-brown solid prepared by passing phosphorus vapour over quicklime heated to dull redness :

$$14P + 14CaO = 5Ca_3P_2 + 2Ca_3P_2O_7.$$

It is used for making *Holmes's signal* for use at sea. This is a sealed tin canister filled with calcium phosphide and attached to a wooden float. The canister is pierced above and below and thrown overboard. The gas ignites spontaneously and burns with a luminous flame.

The formula P_2H_4, analogous to that of hydrazine, is confirmed by the vapour density below atmospheric pressure (m. wt. 66·15). The b.p. (extrapolated) is +51·7°/760 mm., the m.p. −99°. The vapour is unstable and the liquid also decomposes on exposure to light, evolving phosphine and depositing a yellow solid formerly regarded as a solid hydride $P_{12}H_6$ but probably impure amorphous phosphorus : $3P_2H_4 = 2P + 4PH_3$ (Royen and Hill, *Z. anorg. Chem.*, 1936, **229**, 97). The same solid is formed if the uncondensed vapours from the preparation are passed into a flask containing a little fuming hydrochloric acid.

Another solid hydride P_9H_2 was said to be formed by heating $P_{12}H_6$ in vacuum : $5P_{12}H_6 = 6P_9H_2 + 6PH_3$, and another P_8H_2 by the action of very dilute acetic acid on Na_2P_6.

Phosphorus Halides

Phosphorus combines with halogens to form two series of compounds in which it is 3- and 5-valent, PX_3 or PX_5 being formed according as phosphorus or halogen is in excess. Iodine forms PI_3 and P_2I_4, the existence of PI_5 being doubtful, and there is a chloride P_2Cl_4. The physical properties of the halides are :

PF_3 colourless gas, b.p. −95°, m.p. −160°.
PF_5 colourless gas, b.p. −84·5°, m.p. −93·7°.
P_2Cl_4 colourless liquid, b.p. 180°, m.p. −28°.
PCl_3 colourless liquid, b.p. 76°, m.p. −112°, s. g. 1·613 at 0°.
PCl_5 white tetragonal crystals, sublimes at 162·8°, m.p. 166·8° under pressure.
PBr_3 colourless liquid, b.p. 172·9°, m.p. −40°, s. g. 2·885 at 0°.
PBr_5 yellow rhombic crystals, b.p. 106°, decomposes on heating.
P_2I_4 orange red triclinic crystals, m.p. 124·5°.
PI_3 dark red hexagonal crystals, m.p. 61°, b.p. 120° at 15 mm.
Some mixed halides, *e.g.* PCl_4Br and PF_3Cl_2 are known.

Phosphorus trifluoride PF_3 (Moissan, 1884) is formed by the action of arsenic trifluoride on phosphorus trichloride : $PCl_3 + AsF_3 = PF_3 + AsCl_3$; by warming phosphorus tribromide with zinc fluoride : $2PBr_3 + 3ZnF_2 = 2PF_3 + 3ZnBr_2$; and by heating copper phosphide with lead fluoride. The gas does not fume in air and has no action on glass in the cold ; it is hydrolysed by water :

$$PF_3 + 3H_2O = H_3PO_3 + 3HF,$$

and is decomposed by sparking: $5PF_3 = 3PF_5 + 2P$. A mixture of the vapour with oxygen explodes when sparked, the oxyfluoride POF_3 being formed.

Phosphorus pentafluoride PF_5 (Thorpe, 1877) is formed when phosphorus burns in fluorine; when arsenic trifluoride is mixed with phosphorus pentachloride in a freezing mixture: $3PCl_5 + 5AsF_3 = 3PF_5 + 5AsCl_3$; by warming phosphorus fluobromide (made by cooling a mixture of bromine and PF_3 to $-20°$) at $15°$: $5PF_3Br_2 = 3PF_5 + 2PBr_5$; and by heating a mixture of 25 g. of phosphorus pentoxide and 55 g. of powdered fluorspar in an iron tube:

$$6P_2O_5 + 5CaF_2 = 2PF_5 + 5Ca(PO_3)_2.$$

The gas has the normal density corresponding with PF_5, does not attack glass when dry, fumes in air: $PF_5 + H_2O = POF_3 + 2HF$, and combines with ammonia gas to form solid $2PF_5,5NH_3$.

Phosphorus oxyfluoride POF_3 is obtained by heating a mixture of powdered cryolite and phosphorus pentoxide in a brass tube; it is a colourless gas, b.p. $-39{\cdot}8°$, m.p. $-39{\cdot}4°$, which may be collected over mercury. It is also formed by the action of dry hydrogen fluoride on phosphorus pentoxide, and of zinc fluoride on phosphorus oxychloride.

Phosphorus dichloride P_2Cl_4 is an oily fuming liquid formed by the action of a silent discharge on a mixture of PCl_3 vapour and hydrogen (Besson and Fournier, 1910), and by the action of a zinc arc on PCl_3 (Stock, etc., 1925). It is probably $Cl_2 = P - P = Cl_2$.

Phosphorus trichloride PCl_3 is a colourless liquid made by passing a stream of dry chlorine over white or red phosphorus in a retort, and condensing in a cooled dry receiver (Gay-Lussac and Thenard, 1808). It is purified by standing over white phosphorus (which removes excess of chlorine) and redistilling, and may be kept in sealed tubes. The vapour density is normal. The liquid fumes strongly in moist air and reacts violently with water:

$$PCl_3 + 3H_2O = H_3PO_3 + 3HCl.$$

(With a small quantity of water POCl is said to be formed.) It forms $PCl_3,6NH_3$ and $PCl_3,8NH_3$ with ammonia, and reacts violently with sulphur trioxide: $PCl_3 + SO_3 = POCl_3 + SO_2$. It is decomposed by hot concentrated sulphuric acid: $PCl_3 + 2H_2SO_4 = SO_3HCl + SO_2 + 2HCl + HPO_3$, by sulphur chloride: $3PCl_3 + S_2Cl_2 = PCl_5 + 2PSCl_3$, and by liquid hydrogen sulphide (forming phosphorus sulphide).

EXPT. 12.—31 g. of white phosphorus is cut under water into pieces, which are dried between filter paper one at a time and inserted by crucible tongs into a dry tubulated retort previously filled with carbon dioxide. A good cork carrying a leading-in tube which can be moved is fitted to the tubulure of the retort, and the tube attached by rubber tubing to the drying tube of a chlorine apparatus (Fig. 258). The retort is con-

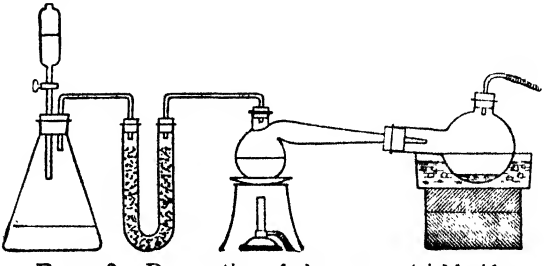


FIG. 258.—Preparation of phosphorus trichloride.

nected with a cooled dry receiver with a calcium chloride tube attached. Chlorine is passed in, the retort not being heated. The phosphorus burns with a pale flame forming PCl_3, which distils over. The stream of chlorine must pass rapidly and steadily; if a white sublimate (PCl_5) forms, lower the inlet tube nearer the phosphorus; if a yellowish-red sublimate forms, raise the tube.

Phosphorus pentachloride PCl_5 (Davy, 1810; Dulong, 1816) is a white or pale greenish-yellow solid formed by burning phosphorus in excess of chlorine or by dropping phosphorus trichloride into dry chlorine: $PCl_3 + Cl_2 = PCl_5$.

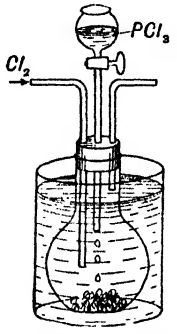


FIG. 259.—Preparation of phosphorus pentachloride.

EXPT. 13.—Allow PCl_3 to drop slowly into a dry flask cooled in ice, through which a stream of dry chlorine is passed. A white powder of PCl_5 collects in the flask (Fig. 259).

Phosphorus pentachloride sublimes without previous fusion when heated below 100° at ordinary pressure. The vapour is dissociated, completely above 300°: $PCl_5 \rightleftharpoons PCl_3 + Cl_2$. The solid melts under pressure when heated in a sealed tube. When volatilised in an atmosphere of PCl_3 vapour the dissociation is repressed (by mass action) and the normal density PCl_5 is found. This is found by volatilising in a Dumas bulb, weighing the mixed vapour, and then analysing the contents of the bulb (Wurtz, *Compt. rend.*, 1873, **76**, 601).

In PCl_5 two atoms of chlorine are very reactive and many metals (Zn, Cd, and even Au and Pt) are converted into chlorides when heated with it:

$$PCl_5 + Zn = PCl_3 + ZnCl_2.$$

In the *vapour* state the molecules PF_5, PCl_5 and PCl_3F_2 are trigonal bipyramids with the phosphorus atom at the centre (Brockway and Beach, *J.A.C.S.*, 1938, **60**, 1836). In *solid* PCl_5 crystals the tetrahedral ions PCl_4^+ and the octahedral ions PCl_6^- are arranged in a tetragonal lattice which may be regarded as a distorted CsCl lattice (Clark, Powell and Wells, *J.C.S.*, 1942, 642).

Phosphorus pentachloride is violently and irreversibly hydrolysed by water. The reaction may proceed in two stages. With a little water, liquid *phosphorus oxychloride* (or phosphoryl chloride) $POCl_3$ is formed (Wurtz, 1847), which is hydrolysed by excess of water to *orthophosphoric acid* (of which it is the acid chloride):

$$PCl_5 + H_2O = POCl_3 + 2HCl$$
$$POCl_3 + 3H_2O = H_3PO_4 + 3HCl.$$

Phosphorus oxychloride is a colourless fuming liquid, b.p. 107·2°, m.p. 1·38°, s. g. 1·712 at 0°, formed by the action of a little water on phosphorus pentachloride and by many other reactions:

(i) By heating a mixture of PCl_5 and P_2O_5 in a sealed tube:

$$3PCl_5 + P_2O_5 = 5POCl_3.$$

(ii) By oxidising PCl_3 with ozone.

(iii) By *gradually* adding 32 g. of powdered potassium chlorate to 100 g. of phosphorus trichloride and distilling (Dervin, 1883) :

$$KClO_3 + 3PCl_3 = 3POCl_3 + KCl.$$

(iv) By heating a mixture of calcium phosphate and carbon at 300–350° in a mixture of chlorine and carbon monoxide (Riban, 1882) :

$$Ca_3(PO_4)_2 + 6CO + 6Cl_2 = 3CaCl_2 + 2POCl_3 + 6CO_2.$$

(v) By distilling phosphorus pentachloride with oxalic acid :

$$PCl_5 + (COOH)_2 = POCl_3 + CO + CO_2 + 2HCl.$$

(vi) By distilling phosphorus pentachloride with boric acid :

$$3PCl_5 + 2H_3BO_3 = 3POCl_3 + B_2O_3 + 6HCl.$$

Phosphorus oxychloride sinks in water and *slowly* dissolves, being hydrolysed : $POCl_3 + 3H_2O = H_3PO_4 + 3HCl$. With water and excess of zinc dust it evolves phosphine (PCl_3 does not).

Phosphorus bromides and iodides.—White phosphorus explodes in contact with liquid chlorine or bromine ; liquid bromine dropped on red phosphorus in a cooled flask reacts with evolution of light and **phosphorus tribromide** PBr_3 distils. By adding bromine to this, yellow solid **phosphorus pentabromide** PBr_5 is formed. The vapour is dissociated : $PBr_5 \rightleftharpoons PBr_3 + Br_2$.

A red form of PBr_5 obtained on slow cooling of the vapour is said (Kastle and Beatty, 1899) to be **phosphorus heptabromide** PBr_7, which is stated to be formed by heating PBr_5 and bromine in a sealed tube at 90°.

Phosphorus oxybromide $POBr_3$ is a colourless crystalline solid, m.p. 56°, b.p. 198°, formed by the action of a little water or of oxalic acid on PBr_5 : it is formed by oxidising PBr_3 (Johnson and Nunn, *J.A.C.S.*, 1941, **63**, 141).

White phosphorus inflames in contact with iodine ; **phosphorus di-iodide** P_2I_4 and **phosphorus tri-iodide** PI_3 are formed by mixing solutions of iodine and white phosphorus in carbon disulphide in the correct ratios and evaporating. PI_5 and POI_3 are not definitely known. The di-iodide is probably $I_2P{\cdot}PI_2$.

Oxides and Oxyacids of Phosphorus

Phosphorus trioxide	P_2O_3 or P_4O_6	**Hypophosphorous acid**	H_3PO_2
Phosphorus tetroxide	P_2O_4 or P_8O_{16}	**Phosphorous acid**	H_3PO_3
Phosphorus pentoxide	P_2O_5 or P_4O_{10}	**Hypophosphoric acid**	$H_4P_2O_6$
		Phosphoric acids :	
		orthophosphoric acid	H_3PO_4
		pyrophosphoric acid	$H_4P_2O_7$
		metaphosphoric acid	HPO_3

The so-called **phosphorus suboxides** P_4O and P_2O are impure red phosphorus. A violet solid said to contain a soluble **phosphorus peroxide** PO_2 is formed by the action of an electric discharge on a mixture of P_2O_5 vapour and oxygen (Schenk and Platz, 1936). Two **perphosphoric acids** H_3PO_5 and $H_4P_2O_8$ and salts are known.

When white phosphorus burns in a free supply of air **phosphorus pentoxide,** first observed by Boyle and called " flowers of phosphorus," is formed. In a limited supply of air some **phosphorus trioxide** is formed. The phosphorus is extinguished before all the oxygen is removed, and part is converted into red phosphorus.

EXPT. 14.—Dry the air inside a tall bell-jar by a capsule of sulphuric acid. After a few hours remove the capsule and replace it by a porcelain crucible supported on a cork, in which a bit of phosphorus is placed. The phosphorus is ignited by touching with a hot wire. Notice the bright flame and the formation of a snow-white powder (P_2O_5) which rapidly settles. After a time the flame becomes larger, greenish, and flickering and P_2O_3 is formed. Red phosphorus remains.

Phosphorus pentoxide is prepared by the combustion of phosphorus in air or oxygen and is very stable even at high temperature (cf. N_2O_5 and As_2O_5).

The apparatus shown in Fig. 260 is used. The sheet-iron cylinder has an opening at the side through which a copper spoon containing burning phosphorus is introduced. The pentoxide settles into the dry bottle below. Several portions of phosphorus are burnt. Air enters between the iron funnel *h* and the cylinder on removing *i*.

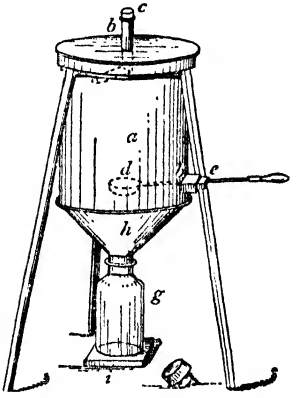


FIG. 260.—Preparation of phosphorus pentoxide.

Commercial phosphorus pentoxide contains some trioxide and metaphosphoric acid. It is purified by volatilising in a current of dry air or oxygen in a hard glass or iron tube, and condensing in a cooled receiver (Chapman and Jones, *J.C.S.*, 1911, **99**, 1811 ; Finch, etc., *ibid.*, 1922, **121**, 692 ; 1926, 117). Lower oxides of phosphorus are oxidised to P_2O_5 by heating at 175°–220° in a current of ozonised air (Manley, *J.C.S.*, 1922, **121**, 331). The purified product, if free from lower oxides, should give no black colour with silver nitrate solution.

The white voluminous powder of phosphorus pentoxide becomes more compact and less volatile at 440°. If distilled in dry carbon dioxide it forms hexagonal crystals subliming at 250°. There are also rhombic and tetragonal forms. The compact variety melts under pressure at 565°, forming a vitreous mass (Hill, Faust and Hendricks, *J.A.C.S.*, 1943, **65**, 794). The vapour density at 1400° is a little higher than corresponds with P_4O_{10} (Tilden and Barnett, *J.C.S.*, 1896, **69**, 154 ; West, *ibid.*, 1902, **81**, 923 ; for the structure of P_4O_{10} see p. 613).

Phosphorus pentoxide shows strong phosphorescence after illumination, especially at low temperatures. It has a powerful affinity for water, becoming moist and sticky on exposure to air from formation of metaphosphoric acid, and it withdraws the last traces of moisture from gases. When thrown into water it reacts with a hissing noise and flocks of metaphosphoric acid separate : $P_2O_5 + H_2O = 2HPO_3$. On standing in the cold these slowly dissolve ; the

metaphosphoric acid hydrates to pyrophosphoric acid and this slowly to orthophosphoric acid; the changes occur rapidly on boiling (Holt and Myers, *J.C.S.*, 1911, **99**, 384). Phosphorus pentoxide withdraws the elements of water from oxyacids, forming the acid anhydrides, *e.g.* SO_3 from H_2SO_4, N_2O_5 from HNO_3, and Cl_2O_7 from $HClO_4$.

Orthophosphoric acid.—The natural mineral phosphates and bone-ash contain salts of orthophosphoric acid H_3PO_4, and the fertiliser *guano* (excreta of sea-birds) is rich in phosphates and combined nitrogen. Another source of fertiliser phosphate is the *basic slag* of steel furnaces, containing $Ca_4P_2O_9$. The acid was prepared by Marggraf in 1743 from phosphorus by combustion. He also noticed that phosphorus increases in weight on combustion, but did not explain this result, which was reinvestigated by Lavoisier in 1772–77. Scheele obtained the acid by oxidising phosphorus with nitric acid.

Commercial orthophosphoric acid is prepared by digesting bone-ash with diluted sulphuric acid, s. g. 1·5, for several hours: $Ca_3(PO_4)_2 + 3H_2SO_4 = 3CaSO_4 + 2H_3PO_4$. The calcium sulphate is filtered off and the phosphoric acid evaporated to s. g. 1·7 (85 p.c. H_3PO_4). The product is impure, and contains acid calcium phosphate $CaH_4(PO_4)_2$. Phosphoric acid is also made by a furnace process (p. 591), air being admitted to burn the phosphorus vapour to P_2O_5, and CO to CO_2; water is sprayed into the cooled gas and crude 85 p.c. phosphoric acid is separated by electrostatic precipitation. The reduction may be carried out in a blast furnace (Curtis, 1935–8).

Pure orthophosphoric acid is obtained from phosphorus pentoxide and water or by oxidising phosphorus with nitric acid:

$$P_4 + 10HNO_3 + H_2O = 4H_3PO_4 + 5NO + 5NO_2.$$

EXPT. 15.—Place 112 c.c. of concentrated nitric acid and 183 c.c. of water in a 2-litre R.B. flask with a boiling tube, through which cold water is passed, hanging in the neck to serve as a reflux condenser. Add 31 g. of red phosphorus in portions of one-fifth at a time, warming till red vapours appear and cooling if the reaction is too violent. When all the phosphorus is dissolved (neglect any black residue), add 20 c.c. of concentrated nitric acid and heat in a porcelain dish to oxidise phosphorous acid. When reaction ceases and a little of the diluted liquid gives no black precipitate with $AgNO_3$ (due to H_3PO_3) add an equal volume of water and filter if necessary. Evaporate in a porcelain dish over a small flame till a thermometer in the liquid rises just to 180°. Cool in a vacuum desiccator over concentrated sulphuric acid, placing the desiccator in a freezing mixture of ice and salt in a sink. Deliquescent crystals of orthophosphoric acid slowly deposit. If the temperature is carried beyond 180° in the evaporation some metaphosphoric acid is formed, and crystallisation will not occur.

The rhombic crystals of orthophosphoric acid melt at 38·6°–42·3° and are very soluble in water. Two crystalline hydrates, $2H_3PO_4,H_2O$ and $10H_3PO_4,H_2O$, were described, but Ross and Jones (*J.A.C.S.*, 1925, **47**, 2165) could not obtain them.

Orthophosphoric acid is *tribasic* and forms three series of salts:

primary, *e.g.* KH_2PO_4; ***secondary***, *e.g.* Na_2HPO_4; ***tertiary***, *e.g.* Na_3PO_4.

Ortho-phosphates are usually called simply "phosphates." Ordinary sodium phosphate is the secondary salt, $Na_2HPO_4,12H_2O$; the tertiary phosphate is $Na_3PO_4,12H_2O$ (p. 312).

The alkali phosphates (except lithium phosphate Li_3PO_4) are soluble in water. The tertiary phosphates of the remaining metals are insoluble in water but dissolve in dilute mineral acids: $Ca_3(PO_4)_2 + 6HCl \rightleftharpoons 3CaCl_2 + 2H_3PO_4$. They are reprecipitated by adding ammonia.

The common primary phosphate is KH_2PO_4, as the sodium salt does not crystallise well. The alkali primary phosphates are acid to litmus, the secondary phosphates faintly alkaline (practically neutral), and the tertiary phosphates strongly alkaline:

$$H_2PO_4' \rightleftharpoons HPO_4'' + H^{\cdot}$$
$$HPO_4'' + H^{\cdot} + OH' \rightleftharpoons H_2PO_4' + OH'$$
$$PO_4''' + H^{\cdot} + OH' \rightleftharpoons HPO_4'' + OH'$$

On titration with litmus phosphoric acid behaves as dibasic; methyl orange changes colour at the stage NaH_2PO_4 and phenolphthalein at the stage Na_2HPO_4 (see Fig. 94); the changes are sharp at 55°. The dissociation constants of orthophosphoric acid are (Britton, *J.C.S.*, 1927, 614):

$$K_1 = [H^{\cdot}]\,[H_2PO_4']/[H_3PO_4] = 9{\cdot}4 \times 10^{-3}$$
$$K_2 = [H^{\cdot}]\,[HPO_4'']/[H_2PO_4'] = 1{\cdot}4 \times 10^{-7}$$
$$K_3 = [H^{\cdot}]\,[PO_4''']/[HPO_4''] = 2{\cdot}7 \times 10^{-12}$$

Solutions of *ortho*-phosphates with excess of nitric acid and ammonium molybdate solution slowly deposit *in the cold* a canary-yellow precipitate of **ammonium phosphomolybdate**, readily soluble in ammonia.

Pyro- and meta-phosphates do not give this reaction unless heated or allowed to stand for a *long* time, when they are converted into orthophosphoric acid. Arsenic acid gives a similar precipitate but *only on heating*. The precipitation of orthophosphoric acid occurs much more rapidly at 60°–65°.

Magnesia mixture (a solution containing magnesium chloride, ammonium chloride and ammonia) gives with orthophosphates a white crystalline precipitate of **magnesium ammonium phosphate** $MgNH_4PO_4,6H_2O$. Orthophosphates give a yellow precipitate of Ag_3PO_4 with silver nitrate solution, but no precipitate with barium chloride, unless the solution is alkaline.

Pyrophosphoric acid is slowly formed (with a little metaphosphoric acid) when orthophosphoric acid is heated at 213° (rapidly above 240°):

$$2H_3PO_4 = H_4P_2O_7 + H_2O.$$

If ordinary sodium phosphate is heated above 240° it loses water and forms **sodium pyrophosphate** (Clark, 1827): $2Na_2HPO_4 = Na_4P_2O_7 + H_2O$.

Lead nitrate solution with this gives a white precipitate of lead pyrophosphate $Pb_2P_2O_7$, and with hydrogen sulphide solution this gives a solution of pyrophosphoric acid: $Pb_2P_2O_7 + 2H_2S = H_4P_2O_7 + 2PbS$. Pure pyrophos-

phoric acid is best obtained by gently heating a mixture of orthophosphoric acid crystals and phosphorus oxychloride: $5H_3PO_4 + POCl_3 = 3H_4P_2O_7 + 3HCl$, evaporating in a vacuum desiccator and cooling at $-10°$ for some time, when white granular crystals of $H_4P_2O_7$, m.p. 61°, separate (Giran, *Compt. rend.*, 1902, **135**, 961). A crystalline hydrate $2H_4P_2O_7,3H_2O$ is described.

Pyrophosphates give a white precipitate of $Ag_4P_2O_7$ with silver nitrate, but no precipitate with barium chloride except in alkaline solution. Magnesium pyrophosphate is formed on heating magnesium ammonium phosphate: $2MgNH_4PO_4 = Mg_2P_2O_7 + 2NH_3 + H_2O$.

If a solution of pyrophosphoric acid is kept for some time or is boiled orthophosphoric acid is formed: $H_4P_2O_7 + H_2O = 2H_3PO_4$, but the salts are very stable in solution.

Pyrophosphoric acid is tetrabasic and is stronger than orthophosphoric acid;

$$K_1 = [H^+]\,[H_3P_2O_7^-]/[H_4P_2O_7] = 1{\cdot}4 \times 10^{-1}$$
$$K_2 = [H^+]\,[H_2P_2O_7^{--}]/[H_3P_2O_7^-] = 1{\cdot}1 \times 10^{-2}$$
$$K_3 = [H^+]\,[HP_2O_7^{---}]/[H_2P_2O_7^{--}] = 2{\cdot}9 \times 10^{-7}$$
$$K_4 = [H^+]\,[P_2O_7^{----}]/[HP_2O_7^{---}] = 3{\cdot}6 \times 10^{-9}$$

Only two series of salts are common, the normal salts $M_4P_2O_7$ and the diacid salts $M_2H_2P_2O_7$. Examples are $Na_4P_2O_7,10H_2O$ (monoclinic), $Na_2H_2P_2O_7$ (hexagonal), $Ca_2P_2O_7,4H_2O$ (amorphous), $Ag_4P_2O_7$ (insoluble), and $Ag_2H_2P_2O_7$ (soluble). The intermediate salts $NaH_3P_2O_7$ and $Na_3HP_2O_7$ have been described but are doubtful, the substances being possibly polyphosphates. Complex ions containing metals (Ag, Zn, Pb, etc.) are formed by dissolving the insoluble metal pyrophosphates in alkali pyrophosphate solution.

Pyrophosphoryl chloride $O(POCl_2)_2$ is a colourless strongly fuming liquid, formed by the action of liquid nitrogen dioxide on phosphorus trichloride, or by the action of phosphorus pentoxide on phosphorus pentachloride:

$$3P_2O_5 + 4PCl_5 = 5O(POCl_2)_2.$$

With excess of phosphorus pentachloride it forms phosphorus oxychloride:

$$O(POCl_2)_2 + PCl_5 = 3POCl_3.$$

It is hydrolysed to orthophosphoric acid: $O(POCl_2)_2 + 5H_2O = 2H_3PO_4 + 4HCl$.

Metaphosphoric acid is formed as a sticky mass when ortho- or pyrophosphoric acid is heated at 316° (best in a gold crucible) (Graham, 1833): $H_3PO_4 = HPO_3 + H_2O$, or by heating ammonium phosphate: $(NH_4)_2HPO_4 = HPO_3 + 2NH_3 + H_2O$. By prolonged heating to redness some phosphorus pentoxide seems to be formed, as the hard glass obtained on cooling crackles when thrown into water (Berzelius). The water content of the residue depends on the duration of heating and pyrophosphoric acid is formed as an intermediate product. At a white heat the acid volatilises and the vapour density corresponds with $(HPO_3)_2$ (Tilden and Barnett, *J.C.S.*, 1896, **69**, 158). The freezing point of a solution of the glass in water shows that the acid is polymerised, $(HPO_3)_n$, whilst the acid in the solution prepared from lead metaphosphate and hydrogen sulphide has the simple formula HPO_3.

Holt and Myers (*J.C.S.*, 1911, **99**, 384; 1913, **103**, 532) by freezing-point measurements distinguished four varieties of metaphosphoric acid: (1) HPO_3 from the lead salt and H_2S, (2) the "crackling" acid, (3) the brittle non-deliquescent glass prepared by heating (2) to redness for twenty-four hours, $(HPO_3)_2$, and (4) the deliquescent glass obtained by heating the commercial acid for a short time, $(HPO_3)_3$.

Pure metaphosphoric acid is best obtained (Geuther, 1874) by the action of phosphorus oxychloride on crystalline ortho- or pyrophosphoric acid:

$$2H_3PO_4 + POCl_3 = 3HPO_3 + 3HCl$$
$$2H_4P_2O_7 + POCl_3 = 5HPO_3 + 3HCl.$$

Metaphosphoric acid (unlike the other phosphoric acids) at once coagulates albumin (white of egg) and gives a white precipitate with barium chloride in *acid* solution. Silver nitrate gives a white amorphous precipitate of $AgPO_3$ from a nearly neutralised solution.

Sodium metaphosphate, probably the hexametaphosphate $(NaPO_3)_6$, is formed as a clear glass when acid sodium orthophosphate, acid sodium pyrophosphate, or microcosmic salt is heated to redness:

$$NaH_2PO_4 = NaPO_3 + H_2O$$
$$Na_2H_2P_2O_7 = 2NaPO_3 + H_2O$$
$$NaNH_4HPO_4 = NaPO_3 + NH_3 + H_2O.$$

The metaphosphates are more numerous than the simple formula HPO_3 for the acid would suggest. Fleitmann and Henneberg (1848) regarded them as derived from polymerised metaphosphoric acids $(HPO_3)_n$, where $n = 1, 2, 3, 4$ and 6. By heating NaH_2PO_4 at 315° Graham (1833) obtained a sparingly soluble metaphosphate, usually called *Maddrell's salt* (1847) and regarded as the **monometaphosphate** $NaPO_3$. On further heating this gives a soluble **trimetaphosphate** $(NaPO_3)_3$, and a soluble **tetrametaphosphate** $(NaPO_3)_4$. When fused and rapidly cooled the metaphosphate forms a clear glass, m.p. 640°, also obtained by heating microcosmic salt; this is called *Graham's salt*, is very soluble, and is the **hexametaphosphate** $(NaPO_3)_6$. From freezing-point and conductivity measurements Tammann (1890) concluded that it is complex, $Na_2[Na_4(PO_3)_6]$. It is used under the name *calgon* for softening water; the calcium is not precipitated but forms a complex ion which does not precipitate soap:

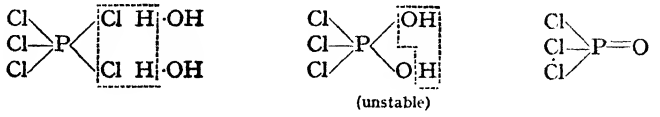
$$Na_2[Na_4(PO_3)_6] + CaSO_4 = Na_2[Na_2Ca(PO_3)_6] + Na_2SO_4.$$

When Maddrell's salt or the tetrametaphosphate is carefully heated, a crystalline salt melting above 800° called *Kurrol's salt* (1892) is formed; it is supposed to be the **octametaphosphate** $(NaPO_3)_8$. Pascal (*Bull. Soc. Chim.*, 1923, **33**, 1611; 1924, **35**, 1119, 1131), who prepared momomeric $NaPO_3$ by the action of sodium ethoxide on the ester $(C_2H_5PO_3)_6$, regarded Maddrell's salt as dimeric, $(NaPO_3)_2$.

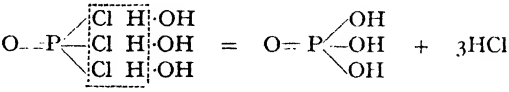
Polyphosphates, *e.g.* $Na_5P_3O_{10}$ $(= Na_4P_2O_7 + NaPO_3)$ are prepared by fusing pyro- and metaphosphates together (Partridge, Hicks, and Smith, *J.A.C.S.*, 1941, **63**, 454).

Constitution of phosphoric acids.—From its method of preparation phosphorus oxychloride is given the formula $O{=}P(Cl_3)$ with a double bond between

the phosphorus and oxygen, agreeing with the molecular volume (Masson and Ramsay, *J.C.S.*, 1881, **39**, 50) :



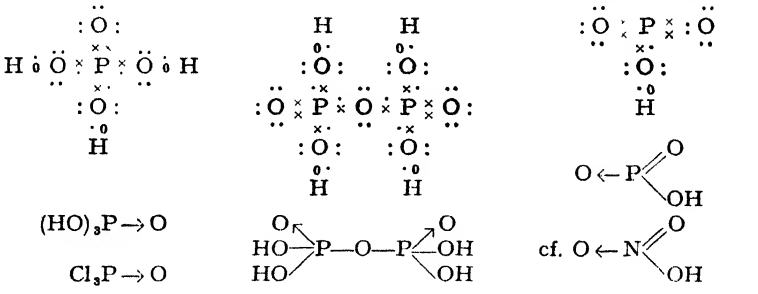
Since orthophosphoric acid is formed by the action of water on phosphorus oxychloride it probably contains the phosphoryl radical $\equiv P=O$:



In non-ionic reactions all three hydroxyl groups of orthophosphoric acid are substituted, as in the formation of the ester $O:P(OC_2H_5)_3$.

The electronic formulae of the phosphoric acids have been represented as follows, giving the phosphorus a covalency of four :

I. Orthophosphoric II. Pyrophosphoric III. Metaphosphoric



also $Cl_3P\rightarrow O$

Phosphorus, unlike nitrogen, may have a covalency of five (as in PF_5, PCl_5, etc.), and the bond distances show that the older formulae with double bonds are nearer the truth than these giving the octet structure, which have generally been adopted (Pauling, *The Nature of the Chemical Bond*, 1940, 240 f.).

Perphosphoric acids.—Phosphates may crystallise with hydrogen peroxide : those with an acid reaction, such as primary phosphates (NaH_2PO_4, etc.), either do not react or form very unstable compounds ; tertiary phosphates, with an alkaline reaction (K_3PO_4, etc.) decompose hydrogen peroxide ; but the secondary phosphates and pyrophosphates of alkali metals give fairly stable crystalline compounds, *e.g.* $K_2HPO_4,2\frac{1}{2}H_2O_2$, $K_4P_2O_7,3H_2O_2$, $CaHPO_4$, $\frac{1}{2}H_2O_2$, $(NH_4)_2H_2P_2O_7,H_2O_2,2H_2O$. These compounds are not true perphosphates. True perphosphates, which do not give reactions of hydrogen peroxide, are obtained in solution by the electrolysis of secondary phosphates of potassium, rubidium, caesium and ammonium in presence of fluorides and chromates, but not from lithium or sodium salts. They oxidise acidified manganous salt solutions to pink permanganic acid and give a black precipitate with silver nitrate solution. These are salts of **perdiphosphoric acid**, $H_4P_2O_8$, and

permonophosphoric acid, H_3PO_5 (Husain and Partington, *Trans. Faraday Soc.*, 1928, **24**, 235).

Solutions supposed to contain H_3PO_5 and $H_4P_2O_8$ are formed by the action of 30 p.c. hydrogen peroxide at low temperatures on phosphorus pentoxide, and on a large excess of pyrophosphoric acid, respectively (Schmidlin and Massini, 1910; d'Ans and Friederich, 1910).

Mono-, di- and **hexafluophosphoric acids**, $H_2[PO_3F]$, $H[PO_2F_2]$ and $H[PF_6]$, are obtained by the action of P_2O_5 on 40 p.c. hydrofluoric acid, and salts are known, *e.g.* $NH_4PO_2F_2$ from P_2O_5 and NH_4F at 130°. The PF_6' ion is very stable towards boiling water and alkali hydroxides. The monofluophosphates are very similar in properties to the sulphates.

Phosphorus trioxide.—The formation of a lower oxide of phosphorus by the slow oxidation of phosphorus in air or its combustion in a limited supply of air was noticed by Sage (1777), but pure phosphorus trioxide was first isolated by Thorpe and Tutton (*J.C.S.*, 1890, **57**, 545; 1891, **59**, 1019). White phosphorus is burnt in a stream of air in a tube, the P_2O_5 also formed is removed by filtration through glass wool, and the phosphorus trioxide vapour is condensed by cooling.

Sticks of phosphorus 1½ in. long are placed in a hard glass tube (Fig. 261) connected with the brass inner tube, 1 in. in diameter and 2 ft. long, of the

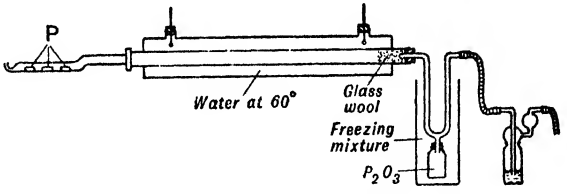


FIG. 261.—Preparation of phosphorus trioxide.

Liebig's condenser containing water at 60°. A plug of glass wool in the brass tube at the end furthest from the phosphorus serves to filter out solid P_2O_5, whilst the P_2O_3 vapour passing on is condensed in the U-tube immersed in ice. A rapid stream of air is aspirated through the apparatus by a water-pump connected with the sulphuric acid wash-bottle, and the phosphorus ignited. The trioxide condensed in the U-tube is melted by warming and runs down into the small bottle beneath. This is the only known method of making P_2O_3. Modifications of the apparatus are described by Stock and Gross (*Ber.*, 1919, **52**, 762) and by Wolf and Schmager (*ibid.*, 1929, **62**, 771).

Pure phosphorus trioxide is a colourless crystalline (monoclinic) solid, m.p. 23·8°, b.p. 173·1°; when impure it is waxy. The vapour density and the depression of freezing point of benzene correspond with P_4O_6.

The P_4O_6 molecule (like that of one form of As_4O_6, p. 626) has the four phosphorus atoms at the corners of a tetrahedron, each linked to three oxygen atoms along the tetrahedron edges (Fig. 262). The P to O distance 1·64 A. indicates a

large amount of double bond character, also shown by the valency angle 125° for P–O–P. In P_4O_{10} an extra oxygen atom is added to each phosphorus atom, completing the PO_4 tetrahedra, these unshared oxygen atoms being very close (1·39 A.) to the phosphorus atoms. In the $P_4O_6S_4$ molecule, which has a similar structure, the P to S distance is short, 1·85 A. (Hampson and Stosick, *J.A.C.S.*, 1938, **60**, 1814; Stosick, *ibid.*, 1939, **61**, 1130).

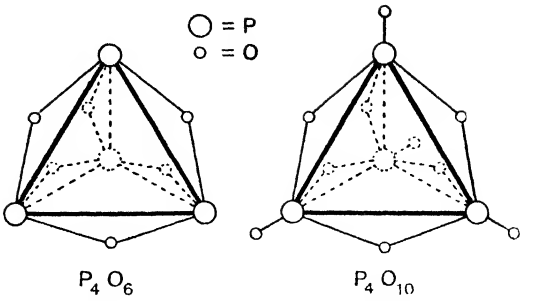


FIG. 262.—Structure of oxides of phosphorus.

Unless quite pure, phosphorus trioxide slowly turns red in light owing to the conversion of white phosphorus contained as an impurity into red phosphorus, and it may be purified by repeated exposure to light and sublimation; when quite pure it does not glow in air (C. C. Miller, 1929). It has a pungent acid smell and is very poisonous. It oxidises in air or oxygen to the pentoxide, inflames at 70° in air and at 50° in oxygen, and spontaneously in chlorine, forming $POCl_3$ and another product supposed to be metaphosphoryl chloride PO_2Cl, or a mixture of $P_2O_3Cl_4$ and $P_7O_{15}Cl_5$. It dissolves slowly in cold water, forming phosphorous acid: $P_2O_3 + 3H_2O = 2H_3PO_3$; with hot water an explosive reaction occurs, with formation of phosphine, phosphoric acid, and red phosphorus: $2P_2O_3 + 6H_2O = PH_3 + 3H_3PO_4$. Alkalis act similarly. Phosphorus trioxide combines violently with sulphur to form crystalline $P_4O_6S_4$.

Phosphorus trioxide inflames in contact with alcohol, but dissolves without decomposition in ether, carbon disulphide, benzene and chloroform. With ammonia it probably forms the diamide of phosphorous acid $HO{\cdot}P(NH_2)_2$.

Phosphorus tetroxide.—Liquid phosphorus trioxide heated in a sealed tube is stable up to 200°; at 210° it becomes turbid, and at 440° a sublimate of phosphorus tetroxide (or dioxide) and a residue of red phosphorus are formed: $2P_4O_6 = 3P_2O_4 + 2P$. The tetroxide sublimes in vacuum at 180°. The vapour density at 1400° corresponds with P_8O_{16}. If phosphorus is burnt in a limited supply of air in a tube a buff-coloured powder deposits on the cooler part, which is a mixture of red phosphorus, P_2O_5 and P_2O_3. On heating in a sealed tube at 290° this gives a crystalline sublimate of phosphorus tetroxide: $P_2O_3 + P_2O_5 = 2P_2O_4$. With water P_2O_4 gives a mixture of phosphorous and phosphoric acids:

$$P_2O_4 + 3H_2O = H_3PO_3 + H_3PO_4$$

(Thorpe and Tutton, *J.C.S.*, 1886, **49**, 833; 1891, **59**, 1019).

A **suboxide** of phosphorus P_2O, said to be formed as a yellow powder by heating phosphorous acid and phosphorus trichloride, is impure amorphous phosphorus (Chalk and Partington, *J.C.S.*, 1927, 1930). Another suboxide P_4O, said to be formed as a red powder by exposing sticks of phosphorus in phosphorus

trichloride to air, by adding an acid to a solution of white phosphorus in alcoholic potash, and by other methods, is also impure amorphous phosphorus (Chapman, etc., *J.C.S.*, 1899, **75**, 973 ; 1901, **78**, 1235).

Phosphorous acid is formed when phosphorus trioxide is dissolved in *cold* water, but is most conveniently prepared by the action of water on phosphorus trichloride (Davy, 1812) : $PCl_3 + 3H_2O = H_3PO_3 + 3HCl$.

To minimise the rise in temperature the trichloride may be added to concentrated hydrochloric acid, when hydrogen chloride gas is evolved and the heat of solution of this does not appear. The solution is evaporated until the temperature rises to 180°, when hydrogen chloride is driven off, and the phosphorous acid crystallised by cooling. The crystalline acid is also obtained by heating phosphorus trichloride with oxalic acid crystals until frothing ceases, and cooling (Hurtzig and Geuther, 1859) : $PCl_3 + 3(COOH)_2 = H_3PO_3 + 3CO + 3CO_2 + 3HCl$.

Phosphorous acid forms white deliquescent crystals, m.p. 73·6°, decomposing at 200° into phosphine and phosphoric acid : $4H_3PO_3 = PH_3 + 3H_3PO_4$; in air the phosphine burns with bright flashes.

Phosphorous acid is a fairly strong reducing agent, precipitating some metals, such as gold and silver, from solutions of their salts, and reducing mercuric to mercurous chloride :

$$2AgNO_3 + H_3PO_3 + H_2O = 2Ag + 2HNO_3 + H_3PO_4$$
$$2HgCl_2 + H_3PO_3 + H_2O = Hg_2Cl_2 + 2HCl + H_3PO_4.$$

On boiling with excess of phosphorous acid, some of the mercurous chloride is reduced to mercury :

$$Hg_2Cl_2 + H_3PO_3 + H_2O = 2Hg + 2HCl + H_3PO_4.$$

Silver nitrate with a phosphite gives first a white precipitate of silver phosphite, Ag_2HPO_3, which soon turns black from formation of silver :

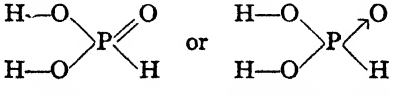
$$Ag_2HPO_3 + H_2O = 2Ag + H_3PO_4.$$

Phosphorous acid precipitates sulphur from sulphurous acid (some $H_2S_5O_6$ is also formed) :

$$SO_2 + 2H_3PO_3 = 2H_3PO_4 + S.$$

It is slowly oxidised by iodine and by permanganate in solution.

Phosphorous acid is *dibasic* (Wurtz, 1845) ; although normal esters $P(OR)_3$ are known the ordinary salts are M_2HPO_3, where M is a univalent metal. The dibasic character is explained by the formulation :



the reducing properties being due to the hydrogen atom directly attached to the phosphorus. The acid is rather weak :

$$K_1 = [H^+]\,[H_2PO_3^-]/[H_3PO_3] = 0{\cdot}05$$
$$K_2 = [H^+]\,[HPO_3^{--}]/[H_2PO_3^-] = 2{\cdot}4 \times 10^{-5}.$$

The two series of phosphites known are MH_2PO_3 and M_2HPO_3. When boiled with alkalis they do *not* evolve hydrogen (cf. hypophosphites) but they evolve phosphine with zinc and dilute hydrochloric acid. Ordinary sodium phosphite is $Na_2HPO_3,5H_2O$. An acid salt $2NaH_2PO_3,5H_2O$, a calcium salt $2CaHPO_3,3H_2O$, an acid calcium salt $CaH_4(PO_3)_2,H_2O$, and hydroxylaminium $(NH_4O)_2HPO_3$, and hydrazinium $(N_2H_6)HPO_3$, phosphites, are known.

Phosphorous acid reacts with phosphorus pentachloride in the normal manner: $H_3PO_3 + 3PCl_5 = PCl_3 + 3POCl_3 + 3HCl$.

Pyrophosphorous acid $H_4P_2O_5$ is formed in needles, m.p. 38°, by shaking PCl_3 with H_3PO_3 for five hours at 30°–40°, and leaving in a desiccator over KOH and P_2O_5. **Metaphosphorous acid** HPO_2 is formed in feathery crystals by the oxidation of phosphine by oxygen under 25 mm. pressure: $PH_3 + O_2 = HPO_2 + H_2$.

Hypophosphoric acid.—If sticks of phosphorus in glass tubes open at both ends are supported in a glass funnel over water under a bell-jar (Fig. 263), oxidation occurs and fumes sink and dissolve in the water. Dulong (1816) noticed that the acid made in this way, called "Pelletier's phosphorous acid" (1796), differs from ordinary phosphorous acid, and he called it "phosphatic acid." Salzer (1877) found that if the liquid is partly neutralised with soda, sparingly soluble crystals of $Na_2H_2P_2O_6,6H_2O$ slowly separate. If lead nitrate is added to a solution of this, $Pb_2P_2O_6$ is precipitated, and on suspending this in water and passing in hydrogen sulphide, a solution of hypophosphoric acid is obtained, which on evaporation in a vacuum desiccator over sulphuric acid gives crystals of $H_4P_2O_6,2H_2O$, m.p. 62°, which lose water, forming $H_4P_2O_6$, m.p. 70°.

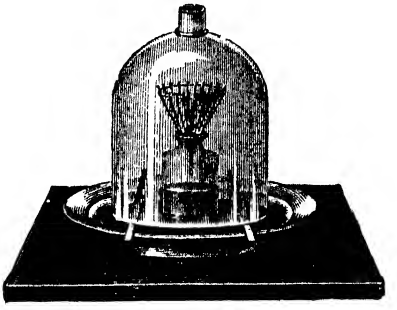


FIG. 263.—Preparation of hypophosphoric acid.

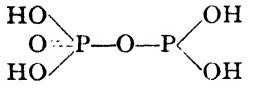
In another preparation (Corne, *J.C.S.*, 1882, **42**, 1264) 6 g. of silver nitrate dissolved in 100 g. of nitric acid diluted with its own volume of water is heated with 9 g. of white phosphorus. When the violent reaction subsides the solution is filtered and cooled, when silver hypophosphate $Ag_4P_2O_6$ separates. This is decomposed by hydrochloric acid to form hypophosphoric acid.

Hypophosphates are formed by the action of bleaching powder or sodium hypochlorite solutions on red phosphorus (Speter, 1927; Probst, 1929), and the acid by oxidising phosphorous acid with iodine (Kolitovska, 1937).

Hypophosphoric acid decomposes on heating: $H_4P_2O_6 = H_3PO_3 + HPO_3$, and at 180° phosphine is evolved. It differs from phosphorous acid in having no reducing action on metallic salts and in not being reduced by nascent hydrogen. The thorium and guanidinium salts are sparingly soluble. The acid is oxidised by hot permanganate, but only slowly by cold.

The doubled formula of the acid $H_4P_2O_6$ is confirmed by the existence of

an acid sodium salt $Na_3HP_2O_6,9H_2O$ and the molecular weight of the ester $(C_2H_5)_4P_2O_6$ (prepared by a special method) in solution (Arbusow and Arbusow, 1931). The structural formula is usually written as :



Hypophosphorous acid.—The residue from the preparation of phosphine by heating white phosphorus with alkali hydroxide solution (p. 598) contains a salt of hypophosphorous acid (Dulong, 1816).

The reaction may be regarded as one of hydrolysis :

$$P_4 + 3OH' = PH_3 + 3PO'$$
$$PO' + H_2O = H_2PO_2'.$$

A solution of barium hypophosphite made by heating white phosphorus with baryta water :

$$2P_4 + 3Ba(OH)_2 + 6H_2O = 2PH_3 + 3Ba(H_2PO_2)_2$$

is filtered from barium phosphate also formed, the excess of baryta is removed by precipitation as barium carbonate by a current of carbon dioxide, and the **barium hypophosphite** is recrystallised as $Ba(H_2PO_2)_2,H_2O$. A solution of barium hypophosphite is precipitated with the calculated amount of dilute sulphuric acid :

$$Ba(H_2PO_2)_2 + H_2SO_4 = BaSO_4 + 2H_3PO_2,$$

and the filtered solution of the acid carefully evaporated below 130° to a syrup, and cooled in a freezing mixture, when it crystallises. A 10 p.c. solution of the acid is made commercially.

Hypophosphorous acid forms colourless crystals, m.p. 26·5°, decomposing at 130°, becoming yellow and evolving phosphine : $3H_3PO_2 = 2H_3PO_3 + PH_3$. The salts also evolve phosphine on heating.

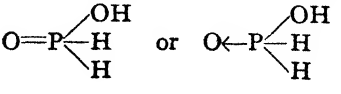
Hypophosphorous acid and hypophosphites are powerful reducing agents, precipitating many metals, *e.g.* silver, from solutions of their salts. Copper salts give on warming a precipitate of cuprous hydride :

$$H_3PO_2 + 2H_2O + 4AgNO_3 = 4Ag + H_3PO_4 + 4HNO_3$$
$$3H_3PO_2 + 3H_2O + 2CuSO_4 = 2CuH + 3H_3PO_3 + 2H_2SO_4.$$

The acid and its salts may be titrated with acid permanganate :

$$H_3PO_2 + 2O = H_3PO_4.$$

Hypophosphorous acid is *monobasic*, forming crystalline salts such as **sodium hypophosphite** NaH_2PO_2,H_2O, and **calcium hypophosphite** $Ca(H_2PO_2)_2$, prepared by heating white phosphorus with sodium hydroxide solution or milk of lime, respectively, and used medicinally as tonics. Most hypophosphites are soluble in water (Th and Bi salts are insoluble). The acid may be formulated :



the reducing properties being due to the two hydrogen atoms directly attached to phosphorus and the acidic properties to the single OH radical.

The H_2PO_2' ion is a distorted tetrahedron with hydrogens at two corners and oxygens at the other two: the P to O distance is 1·5 A. and the angle between the P—O bonds 120°, the P to H distance is 1·5 A. and the angle 92° (Zachariasen and Mooney, 1934).

Phosphorus sulphides.—White phosphorus and sulphur react with explosive violence when fused together, but when a mixture of red phosphorus and small pieces of roll sulphur is heated in a loosely-corked flask reaction commences and proceeds without further heating. According to the proportions taken the phosphorus sulphides P_2S_5, P_4S_7, and P_4S_3 are obtained. A sulphide P_3S_6 has also been described. The pure **pentasulphide** is a pale yellow solid melting at 290° and boiling at 513°–515° giving the normal vapour density; it is slowly hydrolysed by cold water: $P_2S_5 + 8H_2O = 2H_3PO_4 + 5H_2S$. It can be purified by recrystallising from carbon disulphide and heating at 150° in carbon dioxide to remove the solvent. The **trisulphide** P_4S_3 is purified by crystallisation from carbon disulphide or distillation in vacuum. It is bright yellow, melts at 172·5°, boils at 408° giving the normal vapour density, and is only slowly hydrolysed by hot water. The **heptasulphide** P_4S_7 forms slightly yellow crystals, sparingly soluble in CS_2, m.p. 310°, b.p. 523°, rapidly hydrolysed by water.

Thiophosphoric acids.—Sodium salts of **monothiophosphoric acid** H_3PSO_3, **dithiophosphoric acid** $H_3PS_2O_2$ and **trithiophosphoric acid** H_3PS_3O, are formed by adding phosphorus pentasulphide to sodium hydroxide solution and precipitating by alcohol. At 20° the trithiophosphate, at 50° the dithiophosphate $Na_3PS_2O_2,11H_2O$, and at 90° the monothiophosphate $Na_3PSO_3,12H_2O$, are formed. These precipitate barium; barium and strontium; and calcium, barium, and strontium salts, respectively. Magnesium ammonium thiophosphates are sparingly soluble in dilute ammonia. Dithiophosphates give a green colour with manganese and cobalt salts; cobalt monothiophosphate is intensely blue and the nickel salt is bright green.

Thiophosphoryl chloride $PSCl_3$ (Serullas, 1829; Thorpe, 1871; Booth and Cassidy, *J.A.C.S.*, 1940, **62**, 2369) is a colourless fuming liquid, b.p. 125°, formed by the reaction $P_2S_5 + 3PCl_5 = 5PSCl_3$. It is hydrolysed by water:

$$PSCl_3 + 4H_2O = H_3PO_4 + H_2S + 3HCl.$$

Thiophosphoryl fluoride PSF_3 (Thorpe and Rodger, *J.C.S.*, 1888, **53**, 766; 1889, **55**, 306; Booth and Cassidy, *loc. cit.*) is a colourless spontaneously inflammable gas, b.p. −62·6°, formed by the reaction $P_2S_5 + 3PbF_2 = 2PSF_3 + 3PbS$.

Compounds of phosphorus and nitrogen.—Phosphorus pentachloride reacts with dry ammonia gas forming a white solid mixture of substances containing $PCl_3(NH_2)_2$ (Gerhardt, 1846), which is converted by water into **phosphamide** $PO(NH)NH_2$, a white insoluble powder. On heating the product of the action of ammonia on PCl_5 in absence of air, **phospham** $(PN_2H)_x$ remains as a white powder which is only very slowly oxidised on heating to redness in air:

$$PCl_5 + 4NH_3 = PHN_2 + 2NH_4Cl + 3HCl.$$

It is decomposed with incandescence by fused alkali, ammonia and a phosphate

being formed. On heating in absence of air phosphamide gives a white powder of **phosphoryl nitride**: $PO(NH)NH_2 = PON + NH_3$.

Ammonium chloride and phosphorus pentachloride at 175°–200° form a mixture of six **phosphonitrile chlorides**: $(PNCl_2)_3$, $(PNCl_2)_4$, $(PNCl_2)_5$, $(PNCl_2)_6$, $(PNCl_2)_7$ and $(PNCl_2)_x$, which are very stable. The main product is $(PNCl_2)_3$, m.p. 114°, b.p. 256°. Ether solutions of these compounds when shaken with water form **metaphosphimic acids**, $[HO(NH : PO)]_n$, stable salts of which, *e.g.* $(NH_4)_3H_3P_3N_3O_6,H_2O$, are known.

Three **phosphorus nitrides** are described. The compound P_3N_5 is formed by heating P_2S_5 at 230° in ammonia and then in a current of hydrogen at a bright red heat. When phospham is heated in vacuum above 400° it yields pure P_3N_5 by the reaction: $3PN_2H = P_3N_5 + NH_3$. P_3N_5 is a white amorphous powder, decomposing into its elements at high temperature in vacuum. It is scarcely affected by boiling water but is completely decomposed into ammonia and phosphoric acid by water at 180°. It inflames when heated in oxygen or chlorine and is decomposed by many metals. P_3N_5 is decomposed by boiling concentrated sulphuric acid:

$$2P_3N_5 + 5H_2SO_4 + 24H_2O = 6H_3PO_4 + 5(NH_4)_2SO_4.$$

In vacuum at 730° it forms PN, which sublimes. PN exists in two forms, a red and a yellow. When the product of the reaction of liquid ammonia and PCl_5 is heated in vacuum at 550° P_4N_6, a white insoluble non-volatile spontaneously inflammable substance is formed: at 750° in vacuum this gives a sublimate of PN (Moureu, etc., 1934–36).

CHAPTER XXI

ARSENIC AND THE FIFTH GROUP METALS

Arsenic

THE red mineral *realgar* As_2S_2 and the yellow mineral *orpiment* As_2S_3 were known to the ancients. Olympiodoros (fifth century) describes *white arsenic* (arsenious oxide As_2O_3) obtained by roasting the sulphide in air, and the element itself was obtained as a sublimate and was used for whitening copper. The composition of white arsenic as the calx (oxide) of " metallic " arsenic was recognised by Brandt in 1733.

Native arsenic occurs in the Harz and in Japan. Compounds which occur are the sulphides realgar and orpiment, the oxide *arsenolite* As_2O_3, *löllingite* $FeAs_2$, *niccolite* NiAs, *chloanthite* $NiAs_2$, *nickel glance* NiAsS, *smaltite* or *tin-white cobalt* $(Co,Ni,Fe)As_2$, *arsenical pyrites* or *mispickel* FeAsS (isomorphous with pyrites FeS_2), and salts of arsenic acid, *pharmacolite* $CaHAsO_4,2H_2O$, *erythrite* or *cobalt bloom* $Co_3(AsO_4)_2,8H_2O$, and *mimetite* $3Pb_3(AsO_4)_2,PbCl_2$. Native sulphur, iron pyrites and other sulphide ores often contain arsenic, and sulphuric acid made from arsenical pyrites may contain 1 p.c. of As_2O_3. Coal smoke, especially in yellow fogs, may contain arsenious oxide, from pyrites in the coal. Traces of arsenic occur in some mineral waters, in the soil (1–60 p.p.m.), in the adult human body (0·1 mg. per kg.), etc. American tobacco (6–30 p.p.m.; Remington, *J.A.C.S.*, 1927, **49**, 1410), and the fresh edible parts of shell-fish (7–90 p.p.m.; Chapman, *Analyst*, 1926, **51**, 548) contain unusually large amounts of arsenic.

In roasting minerals, *e.g. cobaltite*, in metallurgical treatment fumes of arsenious oxide may be evolved and condense in flues as a powder:

$$4CoAsS + 9O_2 = 4CoO + 4SO_2 + 2As_2O_3.$$

This is obtained in larger amounts by roasting arsenical ores such as mispickel in a current of air. Most of the arsenious oxide used is obtained from flue dust in copper, lead and tin smelting, especially in the U.S.A., Mexico and Sweden (where one smelter, on the Gulf of Bothnia, could supply the world requirement of As_2O_3). The crude oxide is sublimed in iron pots to form *white arsenic* (popularly called simply " arsenic "), the commonest arsenic compound.

Most of the arsenic is used in alloys with lead and copper; as arsenite in weed-killer and sheep-dips, and copper, lead and calcium arsenates in sprays; as oxide as a poison for vermin, preserving skins, in glass-making for removing colour, in enamelling, pyrotechny, wood preserving, and making pigments and mordants.

Arsenic.—The element is obtained by heating the trioxide with charcoal in a clay crucible covered with an inverted iron cone, into which the arsenic sublimes as a grey powder: $As_2O_3 + 3C = 2As + 3CO$; or by heating arsenical pyrites or mispickel in a clay tube fitted for half its length with an inner tube

of sheet iron, into which the arsenic sublimes as a nearly white crystalline mass, which is split off by unrolling the iron tube: $FeAsS = FeS + As$. It is purified by subliming from charcoal powder. Arsenic sulphides are not reduced by heating with carbon, but are reduced when heated with potassium cyanide: $As_2S_3 + 3KCN = 2As + 3KCNS$.

EXPT. 1.—Heat a little arsenious oxide in a dry test-tube with dry powdered charcoal and potassium cyanide. A black mirror of arsenic sublimes. On heating, this oxidises to a white sublimate of arsenious oxide.

Arsenic, like phosphorus, exists in **allotropic forms** (the designations α and γ are sometimes interchanged):

(1) **α-arsenic** or **yellow arsenic**, cubic, s. g. 2·026 at 18°, soluble in carbon disulphide, and corresponding with white phosphorus; it is very unstable and readily passes into γ-arsenic.

(2) **β-arsenic** or **black arsenic**, amorphous, s. g. 4·71, insoluble in carbon disulphide, corresponding with amorphous phosphorus, less stable than γ-arsenic.

(3) **γ-arsenic** or **grey arsenic** (" metallic arsenic "), rhombohedral, s. g. 5·73, insoluble in carbon disulphide, and corresponding with metallic phosphorus; it is the stable and common form of arsenic.

Yellow arsenic or **α-arsenic**, first noticed by Bettendorff in 1867, is obtained (similarly to white phosphorus) by quickly cooling arsenic vapour. Arsenic is distilled in a current of carbon dioxide and the gas is passed into a U-tube, where it meets a current of cooled carbon dioxide, and is then passed into cold carbon disulphide, which dissolves the yellow arsenic (8 g. in 100 c.c. at 20°). The solution on evaporation in the dark deposits light yellow regular crystals, which rapidly oxidise in air at room temperature with a faint luminescence and a garlic odour. It rapidly passes into γ-arsenic when exposed to light, even at $-180°$. Yellow arsenic is formed quantitatively by volatilising γ-arsenic in vacuum and cooling the vapour with liquid air. Its molecular weight in carbon disulphide solution corresponds with As_4 (Erdmann and Reppert, *Annalen*, 1908, **361**, 1).

Stannous chloride when heated with a solution of arsenious oxide in hydrochloric acid gives a brown precipitate of arsenic (*Bettendorff's test*), part of which is α-arsenic, soluble in carbon disulphide. The yield is increased if the mixture is shaken with carbon disulphide during the reduction, since the solution of α-arsenic is more stable than the solid.

Black arsenic or **β-arsenic** is formed when grey arsenic is rapidly heated in a glass tube in a current of hydrogen, when it deposits on the cooler part (200°–220°) of the tube as a shining black mirror, some grey arsenic being deposited nearer the heated part (Berzelius, 1844; Kohlschütter, 1913). It is not appreciably oxidised by air even at 80°, but at 360° it passes into γ-arsenic with strong evolution of heat.

Grey arsenic or **γ-arsenic**, the common variety, forms brilliant tin-white rhombohedral crystals with a metallic lustre, and is a fairly good conductor of heat and

electricity. It is isomorphous with metallic phosphorus, tellurium, antimony and bismuth. It does not form an amalgam. It volatilises slowly at 100° and at 450° it sublimes rapidly without previous fusion, forming a colourless vapour, the density of which shows that it contains As_4 molecules. At higher temperatures dissociation occurs : $As_4 \rightleftharpoons 2As_2$. When heated under pressure in a sealed tube grey arsenic melts at 814°.

Grey arsenic is not oxidised in dry air at room temperature, but in moist air it rapidly becomes covered with a blackish-grey film containing arsenic trioxide, which can be removed by heating alone or with a little iodine. It begins to oxidise in air about 200° and at 250°–300° it shows phosphorescence, the temperature at which this appears in *oxygen* depending on the pressure, as in the case of white phosphorus (Emeléus, *J.C.S.*, 1927, 783). At 400° it burns in air with a white flame, which is brilliant in oxygen : $As_4 + 3O_2 = 2As_2O_3$.

EXPT. 2.—Heat 1 g. of arsenic in a current of oxygen in a hard glass tube connected with an empty flask, the exit tube passing to a U-tube packed with glass-wool to retain fumes of arsenious oxide. The arsenic burns with a white flame and white solid arsenious oxide is deposited in the flask.

Powdered arsenic takes fire in chlorine forming $AsCl_3$, and inflames in contact with bromine forming $AsBr_3$. It combines directly with sulphur and phosphorus on heating, but not with nitrogen or carbon. Arsenic forms fusible **arsenides** with most metals ; 0·3–1 p.c. alloyed with lead makes the metal harder and more fusible, and if this fused alloy is poured through a sieve, the drops falling down a tower into water form shot.

Hydrochloric acid dissolves arsenic only in presence of air. Dilute nitric acid has little action in the cold, but slowly oxidises arsenic to arsenious oxide when hot ; concentrated nitric acid rapidly oxidises arsenic to arsenic acid H_3AsO_4, which is rapidly formed, with some $AsCl_3$, with aqua regia. Hot concentrated sulphuric acid is reduced to sulphur dioxide ; unstable arsenious sulphate $As_2(SO_4)_3$ seems to be formed, but decomposes into the trioxide. Arsenic is insoluble in alkali solution but is attacked by fused alkali hydroxide, forming arsenite and hydrogen : $2As + 6NaOH = 2Na_3AsO_3 + 3H_2$; at high temperatures some arsenate is formed :

$$4Na_3AsO_3 = 3Na_3AsO_4 + Na_3As.$$

ARSENIC HYDRIDE

Arsenic trihydride (*arsine*, or *arseniuretted hydrogen*) is not formed from the elements but is produced by the action of *nascent* hydrogen on a dilute solution of an arsenic compound (Proust, 1799). A solution of arsenious oxide is added to a mixture of zinc and dilute sulphuric acid evolving hydrogen : the hydrogen acquires a very unpleasant smell of garlic and burns with a lilac-coloured flame. Scheele discovered arsine in 1775 by the action of arsenic acid solution on zinc. It is formed at the cathode in the electrolysis of a solution of arsenious oxide, by reduction of the solution with sodium amalgam, and by warming a solution of an arsenious compound with zinc or aluminium and sodium hydroxide solu-

tion (*Fleitmann's test*, 1851 ; arsenates and antimony compounds do not give this reaction). *Arsenic hydride is very poisonous.*

Pure arsine is prepared by passing the mixture with hydrogen obtained by the above methods through a tube cooled in liquid air, when it condenses to a colourless liquid, b.p. $-62{\cdot}4°$, m.p. $-116{\cdot}3°$ (Johnson and Pechukas, *J.A.C.S.*, 1937, **59**, 2065). On warming the liquid the pure gas is evolved.

Arsine may also be prepared by the action of dilute hydrochloric acid on zinc arsenide, obtained by heating equal weights of arsenic and zinc in a closed crucible : $Zn_3As_2 + 6HCl = 2AsH_3 + 3ZnCl_2$; by the action of water on sodium arsenide, formed by passing the impure gas over heated sodium : $Na_3As + 3H_2O = AsH_3 + 3NaOH$; by heating sodium formate (dried at 210°) with sodium arsenite : $Na_3AsO_3 + 3HCOONa = 3Na_2CO_3 + AsH_3$; or (most conveniently) by the action of warm water on aluminium arsenide, obtained by heating aluminium powder and powdered arsenic in a covered crucible (Fonzes-Diacon, *Compt. rend.*, 1900, **130**, 1314) : $AlAs + 3H_2O = Al(OH)_3 + AsH_3$. (The reaction may become violent.)

On exposure to light moist arsine rapidly decomposes, with deposition of black shining arsenic, with a little yellow arsenic, but the pure dry gas is stable (Robertson, Fox and Hiscocks, *Proc. Roy. Soc.*, 1928, **120**, 149). It is decomposed by heat into its elements, the reaction beginning at about 230° : $2AsH_3 = 2As + 3H_2$. From the ratio of the volumes of arsine and hydrogen, and the density of arsine, the formula AsH_3 is found (Soubeiran, 1830). Arsine is slightly soluble in water and ether but dissolves readily in turpentine. It does not form compounds analogous to phosphonium compounds.

The Marsh-Berzelius test.—The formation of gaseous arsine by the action of nascent hydrogen on an arsenic compound, and the ready decomposition of arsine by heat, are applied in the very sensitive Marsh-Berzelius test.

Marsh in 1836 used the deposition of arsenic on a cold surface held in the flame of the burning hydrogen containing arsine ; Berzelius (and Liebig) in 1837 passed the gas through a tube heated at one place and obtained an arsenic mirror (Lockemann, *Z. angew. Chem.*, 1905, **18**, 416).

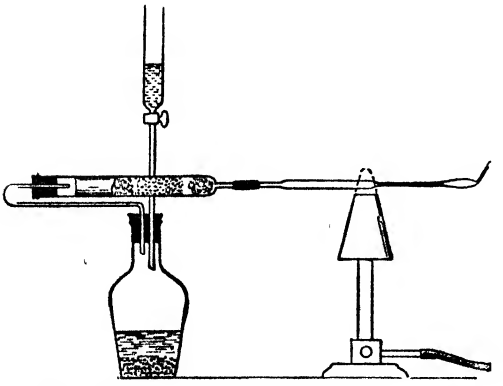


FIG. 264.—Marsh-Berzelius test for arsenic.

EXPT. 3.—Hydrogen generated from pure zinc and pure dilute sulphuric acid is freed from traces of hydrogen sulphide by a roll of dry lead acetate paper in the first part of the drying tube, the second half of which is packed with pure granular calcium chloride, separated from the paper by a plug of cotton-wool (Fig. 264) (*J.S.C.I.*, 1902, **21**, 93 ; 1929, **48**, 226T.). The dry gas passes through a hard glass tube heated at one point to

dull redness. If the materials are free from arsenic, no stain is produced. If a *dilute* solution of arsenious oxide or any material to be tested for arsenic is added to the flask, arsine is formed, which is decomposed in the hot tube, a brown or black mirror being deposited beyond the heated portion. After a sufficient time, all the arsenic is evolved, and by comparing the mirror with standard tubes prepared with known amounts of arsenious oxide (0·001–0·01 mg.) a quantitative estimation may be made. A combination of Marsh's and Bettendorff's (p. 620) tests will detect 10^{-8} g. (Scheucher, *Monatsh.*, 1921, **42**, 411). Some varieties of zinc do not easily reduce arsenic compounds but may be activated by treatment with 2 p.c. cadmium sulphate solution.

If the tube is not heated but the gas kindled at the jet, the flame is tinged lilac and deposits black spots of arsenic on the outer surface of a glazed porcelain dish filled with water: $2AsH_3 = 2As + 3H_2$. These dissolve readily in sodium hypochlorite or bleaching powder solution forming arsenic acid or arsenates: $2As + 5NaOCl + 3H_2O = 2H_3AsO_4 + 5NaCl$, but are insoluble in tartaric acid. If a spot is moistened with yellow ammonium sulphide, and this evaporated by gentle heating, a *bright yellow* spot of As_2S_3 is left.

The *electrolytic Marsh test* (first used by Bloxam in 1861) is now generally used (Aumonier, *J.S.C.I.*, 1927, **46**, 341T.). The mercury cathode, on which arsen*ates* (not reduced at a platinum cathode) also form arsine, is contained in a porous pot, waxed except for a central part and fitted with a rubber stopper carrying a tap-funnel for introducing and withdrawing liquid and a delivery tube connected with a calcium chloride tube and the electrically heated hard glass decomposition tube. The anode is a roll of platinum foil outside the porous cell in a glass vessel. The outer vessel and porous cell contain dilute sulphuric acid. The solution to be tested is added through the tap-funnel (Fig. 265)

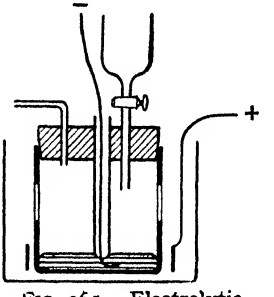


FIG. 265.—Electrolytic Marsh apparatus.

Arsine passed into *dilute* silver nitrate solution gives a black precipitate of silver and the filtrate contains arsenious acid (cf. antimony):

$$AsH_3 + 6AgNO_3 + 3H_2O = H_3AsO_3 + 6HNO_3 + 6Ag.$$

With *more concentrated* silver nitrate solution no precipitate is formed but a yellow solution of a compound of silver arsenide and nitrate:

$$AsH_3 + 6AgNO_3 = Ag_3As,3AgNO_3 + 3HNO_3.$$

On dilution with water, a black precipitate of silver is deposited:

$$Ag_3As,3AgNO_3 + 3H_2O = 6Ag + 3HNO_3 + H_3AsO_3.$$

Arsine with mercuric chloride gives a yellow coloration, due to the formation of $AsH(HgCl)_2$; on further treatment this gives brown $As(HgCl)_3$ and finally black As_2Hg_3. This is the basis of the sensitive **Gutzeit test** (1879).

The solution is added to pure zinc and dilute hydrochloric acid containing a little stannous chloride (to reduce any 5-valent arsenic) in a small bottle fitted with a rubber stopper and a vertical tube containing a roll of lead acetate paper, with a bored rubber stopper at the top. A piece of filter paper previously

moistened with mercuric chloride solution and dried is placed over the hole of the upper stopper and another similar stopper is placed on the top, the two being held together by a spring clip. The yellow stain on the paper is compared with standards.

A *solid arsenic hydride* As_2H_2, noticed by Davy (1810), is said to be formed as a brown powder by (i) the electrolysis of dilute sulphuric acid or sodium hydroxide solution with an arsenic cathode, (ii) the action of water on sodium arsenide, (iii) the action of a silent discharge on arsine, and (iv) by mixing a solution of arsenic chloride in hydrochloric acid with a solution of stannous chloride in ether. Another brown solid hydride As_4H_2 is said (Moser and Brukl, 1924) to be formed by oxidising arsine with a solution of stannic chloride in hydrochloric acid: $4AsH_3 + 5SnCl_4 = As_4H_2 + 10HCl + 5SnCl_2$. The identity of these solid hydrides is doubtful.

By the growth of moulds in presence of arsenic compounds (*e.g.* Scheele's green on wall-paper) a volatile poisonous arsenic compound, trimethylarsine $As(CH_3)_3$, is formed, not arsenic hydride, as was once thought (Challenger and Higginbottom, *J.C.S.*, 1933, 95).

Halogen Compounds of Arsenic

The stable arsenic halides (including the fluoride) are covalent compounds of the type AsX_3, the only definite halide of 5-valent arsenic being AsF_5.

AsF_3 colourless liquid, b.p. 60·4°, m.p. −8·5°, s. g. 2·666 at 0°.
AsF_5 colourless gas, b.p. −53°, m.p. −80°.
$AsCl_3$ colourless liquid, b.p. 130·2°, m.p. −13°, s. g. 2·205 at 0°.
$AsBr_3$ colourless prismatic crystals, m.p. 31°, b.p. 221°, s. g. 3·66 at 15°.
AsI_3 red hexagonal and rhombohedral crystals, m.p. 140·7°, b.p. 394°–414°, s. g. 4·39 at 15°.
As_2I_4 red prismatic crystals, m.p. 130°, b.p. 375°–380°.

Arsenic burns in fluorine to form AsF_3 and AsF_5. **Arsenic trifluoride** AsF_3 (Dumas, 1826), a colourless fuming liquid, is prepared by heating a mixture of arsenious oxide, powdered fluorspar and concentrated sulphuric acid in a lead retort: $As_2O_3 + 6HF \rightleftharpoons 2AsF_3 + 3H_2O$. It is hydrolysed by water.

Arsenic pentafluoride AsF_5 is a colourless gas obtained by distilling a mixture of arsenic trifluoride, antimony pentafluoride and bromine at a temperature not exceeding 55°, and collecting in a receiver cooled in liquid air:

$$AsF_3 + 2SbF_5 + Br_2 = AsF_5 + 2SbBrF_4.$$

Fluoarsenates K_2AsF_7,H_2O and $KAsOF_4,H_2O$ are crystalline solids formed by dissolving potassium arsenate in hydrofluoric acid.

Arsenic trichloride $AsCl_3$ (*butter of arsenic*, Glauber, 1648), the most important halogen compound of arsenic, is formed when arsenic burns in chlorine gas (a reaction which occurs spontaneously even if the materials are very dry), by heating arsenic with mercuric chloride, by heating arsenious oxide in chlorine $11As_2O_3 + 6Cl_2 = 4AsCl_3 + 3(As_2O_5,2As_2O_3)$, or (usually) by distilling a mixture of arsenious oxide, sodium chloride and concentrated sulphuric acid, and condensing the vapour in a cooled receiver: $As_2O_3 + 6HCl \rightleftharpoons 2AsCl_3 + 3H_2O$. The distillate is freed from excess of chlorine by distillation over powdered arsenic.

The most convenient method of preparation is to heat arsenious oxide with sulphur chloride under a reflux condenser, pass chlorine into the mixture, and distil (Partington, *J.C.S.*, 1929, 2573) : $4As_2O_3 + 3S_2Cl_2 + 9Cl_2 = 8AsCl_3 + 6SO_2$.

Arsenic trichloride is a colourless liquid, s. g. 2·2, which in a freezing mixture forms pearly crystals. It fumes in moist air and is hydrolysed by water : the first product is said (Wallace, 1858) to be a crystalline hydroxychloride $AsCl(OH)_2$ but with excess of water arsenious oxide is formed : $2AsCl_3 + 3H_2O \rightleftharpoons As_2O_3 + 6HCl$. The reaction is reversible and arsenic chloride distils when arsenious oxide or an arsenite is boiled with fairly concentrated hydrochloric acid. An arsen*ate* is not decomposed, except with fuming acid. The freezing-point diagram shows no evidence of $AsCl_5$ (Smith and Hora, *J.A.C.S.*, 1904, **26**, 623 ; Kordes, 1927).

Arsenic tribromide $AsBr_3$, a white crystalline solid, less easily hydrolysed than $AsCl_3$, and **arsenic tri-iodide** AsI_3, red crystals, are formed by heating arsenic with a solution of the halogen in carbon disulphide. The tri-iodide is only slightly hydrolysed by water and is precipitated on adding a solution of arsenious oxide in hot hydrochloric acid to a solution of potassium iodide. A **di-iodide** As_2I_4, obtained as a dark red mass by heating iodine with arsenic in a closed tube at 260°, is soluble in CS_2 but is decomposed by water into AsI_3 and arsenic (Hewitt and Winmill, *J.C.S.*, 1907, **91**, 962). AsI and AsI_5 are doubtful.

Oxides and Oxyacids of Arsenic

Two solid acidic *oxides* As_2O_3 and As_2O_5 are known. *Arsenious acid* H_3AsO_3 or $HAsO_2$ is known only in solution but forms solid *arsenites*. Solid *arsenic acids* H_3AsO_4 and $H_4As_2O_7$ and *arsenates* are known.

Arsenious oxide (*arsenic trioxide*) is a white solid, subliming freely at about 193°. The vapour density below 800° corresponds with As_4O_6, at 1800° with As_2O_3. In solution in nitrobenzene the formula is As_4O_6.

Arsenious oxide exists in three forms : (i) an *amorphorous glass*, s. g. 3·738, m.p. 200°, (ii) *octahedral* (the common form), s. g. 3·689, m.p. 275°, b.p. 465°, sublimes above 125° without fusion but melts under pressure, (iii) *monoclinic*, s. g. 3·85, m.p. about 312°.

The *amorphous* variety (first mentioned by Roger Bacon) is a colourless transparent glass formed when the vapour is slowly condensed at a temperature slightly below the point of vaporisation, according to Rushton and Daniels (*J.A.C.S.*, 1926, **48**, 384 ; cf. Schulman and Schumb, *ibid.*, 1943, **65**, 878) at 275°–315°. It may be kept in sealed tubes, but at 100° or in presence of moisture it becomes opaque and very slowly passes into the octahedral form. The solubility (1 part in about 25 parts of water at 13°, or in 12 parts at 100°) decreases on standing, owing to conversion to the octahedral form.

The *octahedral* form is stable under ordinary conditions and is produced when the vapour is *rapidly* condensed, when the trioxide is crystallised from water or hydrochloric acid, or spontaneously with evolution of heat from the vitreous form. Arsenious oxide powder is not easily wetted by water and dissolves only slowly, more rapidly on boiling.

The solubilities of the octahedral form are (Anderson and Storey, *J.A.C.S.*, 1923, **45**, 1102):

	0°	15°	25°	39·8°	62°	98·5°
g./100 g. H_2O -	1·21	1·66	2·05	2·93	4·45	8·18

When 15 g. of As_2O_3 are dissolved by heating in a mixture of 60 c.c. of water and 90 g. of hydrochloric acid of s. g. 1·1, the crystallisation on cooling is accompanied by brilliant flashes of light (Rose, 1835; Bandrowski, *Z. phys. Chem.*, 1895, **17**, 234).

The *monoclinic* variety, which occurs as the mineral *claudetite*, crystallises on cooling from a boiling saturated solution of the amorphous substance in alkali arsenite solution or by sublimation under special conditions.

If arsenious oxide is heated in a sealed tube at 400° the vitreous form remains at the bottom of the tube, the monoclinic form sublimes to the intermediate part at 200°, and the octahedral to the top of the tube. The different forms may be recognised under a lens (Debray, 1864). The transition point of the octahedral and monoclinic varieties is 250° but the change is very slow (Rushton and Daniels, 1926).

The structure of the As_4O_6 molecule is the same as that of P_4O_6 shown in Fig. 262. In the *crystal* the structure of octahedral As_4O_6 (Bozorth, *J.A.C.S.*, 1923, **45**, 1621) is a diamond lattice (p. 440) with tetrahedral As_4O_6 molecules replacing C atoms. The distance As to O in the crystal has increased from that in the vapour molecules (1·80 A.) to 2·00 A., and the bond angle is reduced from 126° to 109° 28′, indicating essentially single bond character $\rangle O$ instead of double bond $\rangle\!\!=\!\!O$ as in the vapour. This comes from the presence of two As atoms of adjacent molecules near each O atom, the electron pairs of which, instead of forming double bonds with As in the same molecule, form weak single bonds with the arsenic atoms of the adjacent molecules.

Arsenious oxide is easily *oxidised* to the pentoxide, arsenic acid or an arsenate, by ozone, hydrogen peroxide, chlorine, aqua regia, bromine, iodine, nitric acid, and hypochlorites (especially in alkaline solution), *e.g.*:

$$As_2O_3 + 2Cl_2 + 5H_2O = 2H_3AsO_4 + 4HCl.$$

It precipitates red cuprous oxide from Fehling's solution.

Arsenious oxide is easily *reduced* to arsenic by heating with charcoal or potassium cyanide, by a solution of stannous chloride, which gives a brown precipitate: $As_2O_3 + 3SnCl_2 + 6HCl = 3SnCl_4 + 2As + 3H_2O$, and by boiling with hydrochloric acid and copper foil, which becomes grey owing to deposition of arsenic: $As_2O_3 + 6HCl + 6Cu = 2As + 6CuCl + 3H_2O$. If the copper foil is washed, dried, and heated in a tube, a crystalline sublimate of arsenious oxide is formed (**Reinsch's test**, 1838). The mere change of colour of the copper is not decisive, as it is also given by selenium, mercury, antimony and bismuth compounds. Arsenates are only slowly reduced.

Arsenious oxide reduces ferric chloride solution on heating:

$$4FeCl_3 + As_2O_3 + 5H_2O = 2H_3AsO_4 + 4FeCl_2 + 4HCl,$$

and arsenites in alkaline solution reduce nitric oxide to nitrous oxide.

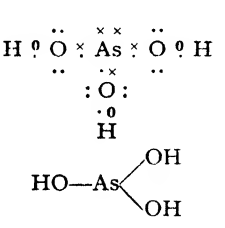
By the action of fuming sulphuric acid and of SO_3 on the trioxide, unstable compounds of As_2O_3 with 1, 2, 3, 4, 6 and 8 SO_3, decomposed by water, are formed : As_2O_3 then acts as a feebly basic oxide (Adie, *J.C.S.*, 1889, **55**, 157).

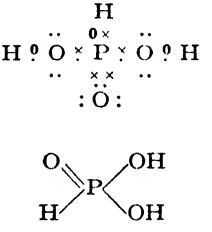
Small quantities of arsenious oxide occur in some mineral waters, which are used as nerve tonics, in skin diseases, and in improving the blood. It is a violent poison : 0·06 g. is a dangerous dose and 0·125–0·25 g. is fatal. The peasants of Styria are said to be able to consume arsenious oxide in amounts (0·3 g.) which would ordinarily be fatal. It is said to act as a cosmetic, to improve the breathing in mountain climbing, and to give plumpness to the figure. Freshly precipitated ferric hydroxide, obtained by adding magnesia to a solution of ferric chloride, adsorbs arsenious oxide and is recommended as an antidote.

Arsenious oxide has only a feeble bactericidal action and some moulds flourish on arsenical solutions.

Arsenious acid and arsenites.—A solution of arsenious oxide in water has a feeble acid reaction and may contain arsenious acid H_3AsO_3 or $HAsO_2$, although only the trioxide crystallises on concentration or on cooling a hot solution. The acid is very weak, the first dissociation constant being $K = 5 \times 10^{-10}$. Arsenious oxide dissolves in solutions of alkali hydroxides or carbonates (when carbon dioxide is evolved ; even warm sodium bicarbonate solution dissolves it), forming **arsenites**, which are not always well defined (cf. Nelson, *J.A.C.S.*, 1941, **63**, 1870). They correspond with the *hypothetical* arsenious acids : *ortho* H_3AsO_3, *pyro* $H_4As_2O_5$, and *meta* $HAsO_2$.

Although the electronic formulae of arsenic compounds are generally analogous to those of phosphorus, arsenious acid is tribasic and its formula is different from that of phosphorous acid, which is dibasic :





Some arsenites which are described are :

ortho-	*pyro-*	*meta-*	*poly-*
K_3AsO_3	$Na_4As_2O_5$	$NaAsO_2$	$K_2As_4O_7$
Ag_3AsO_3	$Ca_2As_2O_5$	$Ca(AsO_2)_2$	$K_6As_4O_9$
$Ca_3(AsO_3)_2$		$Ba(AsO_2)_2$	$Na_{10}As_4O_{11}$
$Pb_3(AsO_3)_2$		$Pb(AsO_2)_2$	

On dissolving arsenious oxide in hot sodium hydroxide solution and evaporating, a white amorphous powder of **sodium arsenite** $NaAsO_2$ is obtained, soluble in and hydrolysed by water. A solution gives with silver nitrate a yellow precipitate of **silver arsenite** Ag_3AsO_3, soluble in acetic acid (the yellow phosphate is insoluble). Copper sulphate gives a bright green precipitate of **cupric arsenite** (*Scheele's green*), $CuHAsO_3$ or $Cu_3(AsO_3)_2,2H_2O$ (Bornemann,

1922), used as an insecticide and formerly as a pigment. When its solution in alkali is boiled, an arsenate is formed and cuprous oxide precipitated: $2Cu^{\cdot\cdot} + AsO_3''' + 4OH' = Cu_2O + AsO_4''' + 2H_2O$. The brilliant *Schweinfurt green* or *Paris green* is a compound of cupric arsenite and acetate, with the formula $Cu(C_2H_3O_2)_2,3Cu(AsO_2)_2$, obtained by adding dilute acetic acid to precipitated copper arsenite, or by boiling basic copper acetate with acetic acid and arsenious oxide, and is used as an insecticide and an oil or water colour.

Arsenic pentoxide and arsenic acid.—Unlike phosphorus, arsenic burns in oxygen to give practically only the lower oxide As_2O_3. Cavendish obtained arsenic acid, corresponding with arsenic pentoxide, in 1764, but did not publish the work, and the acid was independently discovered by Scheele in 1775 by oxidising arsenic trioxide with chlorine water. The acid is usually made by boiling arsenic trioxide with concentrated nitric acid:

$$As_2O_3 + 2HNO_3 + 2H_2O = 2H_3AsO_4 + N_2O_3.$$

The very concentrated solution on cooling deposits rhombic crystals of **ortho-arsenic acid** $2H_3AsO_4,H_2O$ (sometimes H_3AsO_4 separates). At 100° these melt, lose water and leave a crystalline powder of $H_5As_3O_{10}$ or $3As_2O_5,5H_2O$ (Menzies and Potter, *J.A.C.S.*, 1912, **34**, 1452). At 160° slowly, or at 200° rapidly, the acid forms **arsenic pentoxide** As_2O_5, a deliquescent white amorphous solid, which dissolves slowly in water. **Pyroarsenic acid** $H_4As_2O_7$ is obtained in crystals by evaporating a solution of arsenic acid in an open dish until the temperature rises to 170°–180° (Rosenheim and Antelmann, 1930). Meta-arsenic acid is not known. Arsenic pentoxide decomposes at a red heat: $As_2O_5 = As_2O_3 + O_2$.

Arsenic acid is an oxidising agent: it liberates iodine from an iodide in acid solution: $AsO_4''' + 2I' + 2H^{\cdot} = AsO_3''' + I_2 + H_2O$, and with hot *fuming* hydrochloric acid it evolves chlorine (Mayrhofer, 1871): $As_2O_5 + 10HCl = 2AsCl_3 + 2Cl_2 + 5H_2O$.

The **arsenates** are generally isomorphous with phosphates and have similar formulae. The normal ortho-arsenates exist both as solids and in solution, but (unlike the phosphates) the pyro- and meta-arsenates exist only as solids, prepared by heating the appropriate ortho-salts, as in the case of phosphates:

$$2Na_2HAsO_4 = Na_4As_2O_7 + H_2O$$
$$NaH_2AsO_4 = NaAsO_3 + H_2O.$$

Common sodium arsenate $Na_2HAsO_4,12H_2O$ is largely used in calico-printing; calcium, magnesium, manganese and lead ($PbHAsO_4$) arsenates are used as sprays for fruit trees.

Ammonium molybdate and concentrated nitric acid give with arsenates a yellow precipitate similar to that obtained with phosphates, but only on heating. Magnesia mixture gives a white crystalline precipitate of magnesium ammonium arsenate $MgNH_4AsO_4,6H_2O$, similar to $MgNH_4PO_4,6H_2O$. On heating, this gives magnesium pyro-arsenate $Mg_2As_2O_7$.

Arsenates are distinguished from phosphates by giving with silver nitrate in neutral solution a *light chocolate-brown* precipitate of silver arsenate Ag_3AsO_4, soluble in dilute nitric acid and in ammonia. An arsenite present may be detected

by dissolving the precipitate in dilute nitric acid, avoiding excess, and adding ammonia drop by drop. Brown silver arsenate is first precipitated, then yellow silver arsenite.

Arsenic Sulphides

The compounds As_3S, As_2S_2, As_2S_3 and As_2S_5 (the first somewhat doubtful) are known. The disulphide As_2S_2 occurs as the red mineral *realgar*, and the trisulphide As_2S_3 as the yellow mineral *orpiment* (= *auripigmentum*), and they are made by heating arsenic or arsenious oxide with sulphur:

$$2As_2O_3 + 9S = 2As_2S_3 + 3SO_2.$$

The disulphide is not easily made in this way, and an impure product is made by distilling iron pyrites with arsenical pyrites: $2FeAsS + 2FeS_2 = As_2S_2 + 4FeS$. Both sulphides are monoclinic.

Arsenic disulphide or realgar (s. g. 3·506) becomes yellow when exposed to light in air, from formation of As_2S_3 and As_2O_3; it becomes black at 267° owing to conversion into an allotropic form (s. g. 3·254).

Arsenic trisulphide (s. g. 3·43) is formed as a yellow precipitate on passing hydrogen sulphide into a solution of arsenious oxide in dilute hydrochloric acid: $2AsCl_3 + 3H_2S = As_2S_3 + 6HCl$. Orpiment is used as an insecticide. A mixture of the trisulphide and trioxide, made by subliming the trioxide with sulphur, was the pigment *King's yellow*, now replaced by lead chromate.

Realgar and orpiment are used in pyrotechny (*Bengal fire* is a mixture of 2 pts. of realgar, 7 pts. of sulphur and 24 pts. of nitre), and mixed with slaked lime for removing hair; the active agent is probably calcium hydrosulphide, and sodium sulphide is now mostly used instead of the mixture.

Arsenic disulphide and trisulphide burn when heated in air, forming sulphur dioxide and volatile arsenic trioxide. They are almost insoluble in hot concentrated hydrochloric acid (antimony sulphide is readily soluble) but are oxidised by nitric acid.

Arsenic pentasulphide As_2S_5 is formed as a light yellow precipitate when hydrogen sulphide is passed rapidly into a warm solution of arsenic acid containing 10–12 p.c. of free hydrochloric acid (Bunsen, 1878; Brauner and Tomicek, *J.C.S.*, 1888, **53**, 145; Usher and Travers, *ibid.*, 1905, **87**, 1370): $As_2O_5 + 5H_2S = As_2S_5 + 5H_2O$. If the reaction takes place slowly and in the cold, a white precipitate of sulphur is first formed and the arsenic acid is reduced to arsenious acid, which is then precipitated as arsenious sulphide:

$$H_3AsO_4 + H_2S = H_3AsO_3 + H_2O + S$$
$$2H_3AsO_3 + 3H_2S = As_2S_3 + 6H_2O.$$

Arsenic trisulphide dissolves readily in alkali hydroxide or ammonia, and even in warm ammonium carbonate solution (antimony trisulphide is insoluble), forming a mixture of arsenite and **thioarsenite**:

$$As_2S_3 + 6OH' = AsO_3''' + AsS_3''' + 3H_2O.$$

On acidifying, all the arsenic is precipitated as trisulphide:

$$AsO_3''' + AsS_3''' + 6H^{\cdot} = As_2S_3 + 3H_2O.$$

When arsenic trisulphide is dissolved in an alkali sulphide, a thioarsenite alone is formed : $3S'' + As_2S_3 = 2AsS_3'''$.

Thioarsenites are derived from hypothetical thioarsenious acids : H_3AsS_3 (*ortho*), $H_4As_2S_5$ (*pyro*), $HAsS_2$ (*meta*), but (like the arsenites) have not been much investigated (Wünschendorff, 1929 ; *Chem. Abstr.* (Amer.), 1930, **24**, 1815). $(NH_4)_3AsS_3$ and $Ca_3(AsS_3)_2$ form colourless crystals, K_3AsS_3 and Na_3AsS_3 amorphous white powders.

When arsenic trisulphide is boiled with sodium carbonate solution, carbon dioxide is evolved, arsenic disulphide (As_2S_2) precipitated, and a solution of a thioarsenite formed. On fusing the trisulphide with sodium carbonate, arsenic sublimes and the residue contains an arsen*ate* and thioarsen*ate*. Arsenic also sublimes when the sulphide is fused with sodium carbonate and potassium cyanide : it is said that none then remains in the residue.

Arsenious sulphide dissolves in an alkali polysulphide, *e.g.* yellow ammonium sulphide $(NH_4)_2S_2$ to form a **thioarsenate**, also formed when a thioarsenite is digested with sulphur : $AsS_3''' + S = AsS_4'''$. On acidifying, a yellow precipitate is formed which has been described as the pentasulphide or as a mixture of the trisulphide and sulphur. Arsenic trisulphide and sulphur or arsenic pentasulphide when digested with alkali hydroxide form salts containing both oxygen and sulphur ; *e.g.* $Na_3AsO_3S,12H_2O$; K_3AsOS_3 ; $Na_2HAsO_3S,8H_2O$; $Na_3AsO_2S_2,11H_2O$: $As_2S_5 + 6KOH = K_3AsS_4 + K_3AsO_3S + 3H_2O$. These are colourless and are decomposed by acids into arsenic acid and free sulphur or arsenic trisulphide. The thioarsenates are soluble and crystalline ; *e.g.* $Na_3AsS_4,8H_2O$, $(NH_4)_3AsS_4$. By the action of sodium sulphide solution on arsenious oxide in the proportions $2Na_2S : As_2O_3$ a thioarsenate and elementary arsenic are produced.

A **subsulphide** As_3S is said to be formed as a dark brown powder by the action of PCl_3 and SO_2 on sodium arsenite solution, or by the action of sodium hyposulphite ($Na_2S_2O_4$) on an arsenite or arsenate solution (Scott, 1900 ; Farmer and Firth, *J.C.S.*, 1926, 119).

Antimony

A black pigment called *mestem*, used in Egypt before 3000 B.C. for painting the eyebrows, was usually galena (PbS) but sometimes native antimony sulphide (*stibnite*) Sb_2S_3, later called *stimmi* in Greek and *stibium* in Latin. The name *antimonium*, of obscure origin, is used for it by Constantinus Africanus in A.D. 1050. A Chaldaean vase of 3000 B.C. consists of pure metallic antimony, and ancient metal objects from China, Korea and Japan also contain antimony.

Antimony and its compounds were much used by the alchemists, and a monograph, *The Triumphal Chariot of Antimony* (Leipzig, 1604) by " Basil Valentine " (= Thoelde) describes many of them. The Arabic name for finely powdered stibnite, *al kohl*, was used by Paracelsus for spirit of wine, " alcohol."

Metallic antimony, found in Sweden, Borneo, Queensland, etc., and the *oxides* Sb_2O_3 (*valentinite* and *senarmonite*) and Sb_2O_4 (*cervantite*), occur

sparingly ; the only important ore is the sulphide Sb_2S_3, *stibnite*, s. g. 4·64, found in large quantities in China (Hunan province), and somewhat less abundantly in Mexico, Bolivia, Peru, Czechoslovakia, Yugoslavia, etc. It forms rhombic crystals. The ores are difficult to concentrate, but flotation can be used.

Rich ore is *liquated* by heating, when the fusible stibnite (m.p. 548°) flows away from the rock, and the sulphide is reduced by heating with iron and a little salt in plumbago crucibles : $Sb_2S_3 + 3Fe = 2Sb + 3FeS$. The metal (91 p.c.) melts and collects below the slag. It is refined by twice remelting with a little stibnite and salt, and then with a flux made by melting stibnite with potassium carbonate. The purified metal (over 99 p.c.) is called *star antimony*, because of the fern-like crystals on the surface.

Poor ores are roasted, either in a reverberatory furnace at 350° to form non-volatile dioxide Sb_2O_4, or at 400° in a cupola or shaft furnace to form Sb_2O_3 which sublimes and is collected. The oxides are reduced by smelting with charcoal or anthracite, and sodium carbonate and sulphate as a flux.

Antimony is precipitated as a fine black powder by zinc from a solution of the trichloride ; this powder is used in covering plaster casts to give them the appearance of steel.

Pure antimony is made from the pure pentoxide (prepared by the hydrolysis of recrystallised chlorantimonic acid) by fusing with potassium cyanide or heating in a current of hydrogen.

Antimony is silver-white and lustrous, s. g. 6·71, brittle and easily powdered. The fused metal expands slightly on solidification (Matsuyama, 1928) ; on slow cooling it deposits large obtuse rhombohedral crystals, on rapid cooling it is granular. The vapour densities at 1572° and 1640° correspond with molecular weights intermediate between Sb_3 and Sb_2, perhaps $Sb_4 \rightleftharpoons 2Sb_2$; at 2070° it corresponds with Sb. The freezing points of solutions in lead and cadmium correspond with Sb_2 and Sb, respectively. Antimony is a poor conductor of heat and electricity. It is diamagnetic.

Antimony is unchanged by air, water and dilute acids, but it decomposes steam at a red heat and is oxidised by concentrated nitric acid to a white powder of the hydrated pentoxide (" antimonic acid "). The pure metal does not dissolve in concentrated hydrochloric acid, but the commercial metal dissolves on heating. Antimony is attacked by hot concentrated sulphuric acid, forming the sulphate : $2Sb + 6H_2SO_4 = Sb_2(SO_4)_3 + 3SO_2 + 6H_2O$, and it dissolves easily in aqua regia to a solution of the pentachloride $SbCl_5$. It burns spontaneously in chlorine to $SbCl_5$, inflames in contact with bromine, and combines with iodine at room temperature and with sulphur on heating.

When strongly heated in air antimony burns, evolving white fumes of the trioxide. A bead of antimony heated on charcoal before the blowpipe continues to burn when the flame is removed, and if dropped on a piece of paper turned up at the edges the bead breaks into burning globules, which leave curious charred tracks on the paper. The metal burns brilliantly when heated in oxygen, even when very dry.

In addition to the crystalline metal, unstable *amorphous allotropic forms of antimony* are known.

Yellow or **α-antimony** is formed by the action of ozonised oxygen on liquid stibine SbH_3 at $-90°$, or by mixing solutions of stibine and of chlorine in liquid ethane at $-100°$ in red light. It is slightly soluble in carbon disulphide, but is very unstable and above $-90°$ rapidly passes into **black** or **β-antimony**, an amorphous black powder, s. g. 5·3, formed directly from liquid stibine and oxygen at $-40°$, or by rapidly and strongly cooling antimony vapour. Black antimony oxidises spontaneously in air; on warming it forms ordinary antimony with evolution of heat. **Explosive antimony** was obtained by Gore in 1854 by the slow electrolysis of a concentrated solution of antimony trichloride in hydrochloric acid with a platinum cathode and an antimony anode, the metal deposited on the cathode, s. g. 5·25–6·3, having the appearance of polished graphite. When scratched it is explosively converted into ordinary antimony with evolution of heat and fumes of $SbCl_3$, which it always contains to some extent. At 200° it explodes violently. It can be kept under water, but if this is heated to 75° the antimony undergoes change with a hissing noise (Cohen, *J.S.C.I.*, 1929, **48**, 162R.; Stilwell and Audrieth, *J.A.C.S.*, 1932, **54**, 472).

Antimony is a constituent of several important alloys; it forms an amalgam only on heating. A mixture of 15 pts. of antimony and 85 of lead is *hard lead* or *antimonial lead*, used for stopcocks for sulphuric acid. The most important alloys are those with tin and lead, used for type metal; they expand on solidification and give sharp impressions:

	Pb	Sb	Sn	Cu
Type metal - -	55	30	15	—
Britannia metal -	—	5	94	1
Anti-friction metal -	75	15	8	2

The definite compounds $SbCu_2$, a purple alloy (*regulus of Venus*), $SbCu_3$ with a close-packed hexagonal structure, and many other intermetallic compounds, are known. Antimony forms **antimonides** with alkali metals, Li_3Sb, Na_3Sb, NaSb, etc.

Antimony forms two series of compounds, the *antimonous compounds* SbX_3 in which it is 3-valent, and the *antimonic compounds* SbX_5 in which it is 5-valent. Both are stable. The halogen compounds are covalent (although the fluoride forms a conducting solution) and there is little tendency to form salts with oxyacids, the sulphate $Sb_2(SO_4)_3$ being the only one well-defined. The oxides Sb_2O_3 and Sb_2O_4 are amphoteric, but Sb_2O_5 is decidedly acidic. An oxide Sb_2O_4, which may be $(Sb^{III}O)(Sb^{V}O_3)$, and a chloride $SbCl_4$ in solution, forming stable complex salts. *e.g.* Rb_2SbCl_6, are known.

Antimony Hydride

Antimony hydride or *stibine* SbH_3 is a gas formed mixed with hydrogen when a solution of an antimony compound is added to zinc and dilute sulphuric acid (L. Thompson, 1837; Pfaff, 1837). The gas burns with a grey flame, evolving

fumes of antimony oxide, and a black stain of antimony is deposited on a cold porcelain dish held in the flame. A black mirror of antimony is deposited, on both sides of the heated spot, on passing the gas through a heated glass tube. (Arsine is more stable and deposits arsenic only on the side furthest from the generating flask.)

To distinguish the antimony from the similar but brighter arsenic mirror, three spots are formed on a dish, which are treated as follows:

(i) Moisten with bleaching powder solution: As dissolves, Sb is insoluble.
(ii) Moisten with concentrated tartaric acid solution: Sb dissolves, As is insoluble.
(iii) Moisten with yellow ammonium sulphide and evaporate: As gives yellow As_2S_3, Sb gives orange Sb_2S_3.

A good yield of stibine is obtained by dropping a solution of antimony trichloride in 1 : 1 hydrochloric acid into a flask containing zinc and dilute hydrochloric acid (F. Jones, *J.C.S.*, 1876, **29**, 641), or by the action of dilute sulphuric acid on an alloy of equal weights of zinc and antimony. *Pure stibine* (Stock, etc., 1901–08) is prepared by acting with hydrochloric acid on an alloy of magnesium with 33 p.c. of antimony, washing the gas with water, drying with calcium chloride and phosphorus pentoxide, and passing through a tube cooled in liquid air. White solid stibine, m.p. $-88°$, b.p. $-17°$, is formed. On warming this evolves pure stibine, which may be collected over mercury and is fairly stable when dry.

Stibine is formed at an antimony cathode in the electrolysis of an alkali or sulphuric acid solution in a divided cell when the over-voltage exceeds a certain value (Sand, etc., *J.C.S.*, 1923, **123**, 456; 1927, 378): the hydrogen may contain 15 p.c. of SbH_3.

Stibine is fairly soluble in water and very soluble in carbon disulphide. It has an unpleasant smell and is poisonous. It is attacked by air or oxygen, forming water and antimony, and decomposes into its elements when moist, or with explosion when heated or sparked, or sometimes spontaneously, as it is endothermic. The density is slightly higher than corresponds with SbH_3.

Hydrogen containing stibine gives a black precipitate with silver nitrate solution and the filtrate is free from antimony, whilst with arsine the filtrate contains all the arsenic. The precipitate first formed is silver antimonide $SbAg_3$, but this is rapidly decomposed by excess of silver nitrate into a black mixture of silver, antimony trioxide and a little antimony (Lassaigne, 1840):

$$SbH_3 + 3AgNO_3 = Ag_3Sb + 3HNO_3$$
$$2Ag_3Sb + 6AgNO_3 + 3H_2O = 12Ag + Sb_2O_3 + 6HNO_3.$$

If this precipitate is warmed with hydrochloric acid, the filtrate gives with H_2S an orange-red precipitate of Sb_2S_3.

Antimony Halides

Covalent halogen compounds of the type SbX_3 are formed with all the halogens, SbX_5 only with fluorine and chlorine :

SbF_3, white octahedral crystals, m.p. 292°, b.p. 310°.
$SbCl_3$, white rhombic crystals, m.p. 73·2°, b.p. 223·5°.
$SbBr_3$, white rhombic crystals, m.p. 94°, b.p. 280°.
SbI_3, three forms : dark red hexagonal crystals, yellow monoclinic and rhombic crystals, m.p. 171°, b.p. 401°.

SbF_5, colourless liquid, m.p. 6°, b.p. 150°, s. g. 2·99 at 23°.
$SbCl_5$, yellow liquid, m.p. 3°, b.p. 140°, s. g. 2·3356 at 20°.

Antimony trifluoride SbF_3 is formed by distilling antimony with mercuric fluoride, and as it is stable towards water (although somewhat hydrolysed) by dissolving Sb_2O_3 in hydrofluoric acid and evaporating. It forms complex compounds, *e.g.* **potassium fluorantimonite** K_2SbF_5, obtained in colourless crystals by dissolving Sb_2O_3 and KF in hydrofluoric acid, and used in calico-printing as a mordant. The salts $NaHSbF_5$, $KSbF_4$ and $CsSb_2F_7$ are known, and $(NH_4)_2[SbF_3(SO_4)]$, " antimony salt," is also used in dyeing.

Antimony pentafluoride SbF_5 is a colourless oily liquid, without action on glass, obtained by boiling $SbCl_5$ with anhydrous hydrofluoric acid under a reflux condenser for three days, and then fractionating : $SbCl_5 + 5HF = SbF_5 + 5HCl$. The apparatus must be of platinum (Ruff and Plato, 1904–9). Sparingly soluble complex salts, *e.g.* $KSbF_6$ and K_2SbF_7, are formed with alkali fluorides.

Antimony trichloride $SbCl_3$ was prepared by Paracelsus by distilling antimony with mercuric chloride : $2Sb + 3HgCl_2 = 2SbCl_3 + 3Hg$. It may be obtained by the regulated action of chlorine on antimony. Glauber (1648) obtained it by dissolving stibnite in hot concentrated hydrochloric acid : $Sb_2S_3 + 6HCl = 2SbCl_3 + 3H_2S$. The dark brown solution is distilled, when water passes over, then hydrochloric acid, and finally antimony trichloride, which solidifies in the receiver as a white soft crystalline mass (*butter of antimony*). It may be recrystallised from carbon disulphide. The vapour density and the elevation of boiling point in solution in ether correspond with $SbCl_3$.

Antimony trichloride is decomposed by water with precipitation of basic chlorides, but it forms a clear solution with dilute hydrochloric acid. With concentrated hydrochloric acid it forms crystalline **chlorantimonous acid** $HSb_2Cl_7,2H_2O$. Complex salts such as $NaSbCl_4$ and K_2SbCl_5 are known.

Antimonous oxychloride is formed as a white precipitate, formerly called *powder of Algaroth*, on pouring a solution of the trichloride in hydrochloric acid into water. The composition varies with the dilution but is usually taken as $Sb_4O_5Cl_2$. Two definite oxychlorides SbOCl and $Sb_4O_5Cl_2$ are known (Van Bemmelen, *Z. anorg. Chem.*, 1903, **33**, 272 ; Lea and Wood, *J.C.S.*, 1924, **125**, 137) :

$$SbCl_3 + H_2O \rightleftharpoons SbOCl + 2HCl \text{ (with a little water)}$$
$$4SbCl_3 + 5H_2O \rightleftharpoons Sb_4O_5Cl_2 + 10HCl \text{ (with a larger amount of water).}$$

By heating the oxychloride with water in a sealed tube at 150° or boiling with sodium carbonate solution, antimony trioxide is formed.

Fused $SbCl_3$ is a very poor conductor of electricity, but it gives a conducting solution in liquid hydrogen sulphide. A solution in hydrochloric acid may be titrated to the pentachloride with sodium bromate :

$$3SbCl_3 + 6HCl + NaBrO_3 = 3SbCl_5 + NaBr + 3H_2O.$$

Antimony pentachloride is formed by burning antimony in chlorine (H. Rose, 1825) or by the action of chlorine or aqua regia on the trichloride. It is a yellow fuming liquid, which is a non-conductor of electricity but forms a conducting solution in liquid sulphur dioxide. The vapour is slightly dissociated at the boiling point, 140° : $SbCl_5 \rightleftharpoons SbCl_3 + Cl_2$, but the compound boils unchanged at 79° under 22 mm. pressure, and the vapour density at 55 mm. corresponds with $SbCl_5$. With ice-cold water two crystalline hydrates, $SbCl_5,H_2O$ (soluble in chloroform) and $SbCl_5,4H_2O$ (insoluble in chloroform), are obtained. With excess of hot water hydrated antimony pentoxide is formed. With concentrated hydrochloric acid a fairly stable crystalline **chlorantimonic acid** $2HSbCl_6,9H_2O$ is formed, also prepared by passing chlorine into a solution of the trichloride in hydrochloric acid, and adding excess of concentrated hydrochloric acid. Numerous salts derived from H_3SbCl_8, H_2SbCl_7 and $HSbCl_6$ are known.

A compound $SbCl_9$ is indicated on the freezing-point diagram of $SbCl_5$ and Cl_2 (Biltz and Jeep, 1927). Antimony pentachloride combines with many chlorides, oxides, salts, organic compounds, iodine chloride ($SbCl_5,2ICl$ and $SbCl_5,3ICl$), sulphur tetrachloride ($SbCl_5,SCl_4$), etc.

The brown liquid formed by the action of chlorine on $SbCl_3$ appears to contain **antimony tetrachloride** $SbCl_4$ or an acid $H_2Sb^{IV}Cl_6$. Many stable dark-coloured salts, *e.g.* Rb_2SbCl_6, corresponding with this acid, are known, and as they are isomorphous with corresponding stannic, plumbic and platinic compounds they probably contain quadrivalent antimony (Weinland, 1905).

Antimony tribromide $SbBr_3$, which forms white deliquescent needles, is formed from the elements. It is decomposed by water to the oxybromides SbOBr and $Sb_4O_5Br_2$. The pentabromide is not known but **bromantimonic acid** $HSbBr_6,3H_2O$ is formed in dark red, almost black, crystals from a solution of $SbBr_3$ and bromine in concentrated hydrobromic acid, and salts of it and of more complex bromantimonic acids are known (Weinland, 1903).

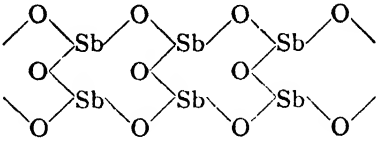
Antimony tri-iodide SbI_3 is formed by warming powdered antimony with a solution of iodine in carbon disulphide and separates in red plates on evaporation. Two other greenish-yellow forms are described. The vapour of SbI_3 is scarlet. On hydrolysis $Sb_4O_5I_2$ is formed as a yellow powder.

Oxides of Antimony

Antimony forms three oxides, Sb_2O_3, Sb_2O_4 and Sb_2O_5, which are stable but are easily reduced by heating with hydrogen or carbon.

Antimony trioxide or *antimonous oxide* Sb_2O_3 or Sb_4O_6 occurs native as *senarmonite*, octahedral, s. g. 5·2, with a diamond lattice like that of As_4O_6

(p. 626), and the commoner rhombic *valentinite*, s. g. 5·67, which contains long strings of atoms linked by covalent bonds (Buerger and Hendricks, 1937):



Antimony trioxide is formed as a white powder (*flowers of antimony*) by burning antimony in air and (mixed with some Sb_2O_4) by roasting stibnite. It is also formed by digesting the oxychlorides SbOCl or $Sb_4O_5Cl_2$ with sodium carbonate solution, and by passing steam over red-hot antimony. A hot solution in sodium carbonate deposits both forms. Antimony trioxide becomes yellow on heating and pale buff on cooling, melts at 656° and boils at 1560°, the vapour density corresponding with Sb_4O_6. It is almost insoluble in water but is soluble in hot concentrated sulphuric acid, and on cooling crystalline **antimony sulphate** $Sb_2(SO_4)_3$ deposits. The oxide dissolves readily in dilute hydrochloric acid forming $SbCl_3$, in tartaric acid, and in alkali solutions forming **metantimonites**, *e.g.* $NaSbO_2$, derived from a hypothetical $HSbO_2$, which are hydrolysed by water.

The sodium salt is sparingly soluble and crystallises in glittering octahedra as $NaSbO_2,3H_2O$; the potassium salt KSb_3O_5, obtained by boiling antimonous oxide with potassium hydroxide solution, is readily soluble. Supposed antimonous acids are probably colloidal hydrated oxide.

Antimony trioxide is used in white paints and enamels, but there is a danger that it may be dissolved from the latter by dilute acids and cause poisoning.

Antimony tetroxide Sb_2O_4 occurs as *cervantite* and is obtained as a white powder by heating the trioxide in air at 700°–910°. At higher temperatures it decomposes into trioxide. Impure Sb_2O_4 obtained as a fused mass by roasting stibnite is called *glass of antimony*; this contains the tetroxide and unchanged stibnite and is used in colouring glass and porcelain yellow. Antimony tetroxide forms salts called **hypoantimonates**, derived from a hypothetical acid $H_2Sb_2O_5$. They are made by fusion with alkalis. The potassium salt $K_2Sb_2O_5$ is sparingly soluble in cold but easily in hot water; if the solution is mixed with hydrochloric acid, $K_2Sb_4O_9$ is precipitated.

Antimony pentoxide Sb_2O_5 is a yellow powder obtained by gently heating the solid formed by the repeated evaporation of antimony with concentrated nitric acid. Above 440° it decomposes into Sb_2O_4, and when prepared as described always contains a little lower oxide. A stable intermediate oxide Sb_6O_{13} is formed at 430° (Simon, 1927).

Antimony pentoxide is almost insoluble but reddens litmus. Various *antimonic acids* described are of indefinite composition, but a compound $3Sb_2O_5,5H_2O$ or $H_5Sb_3O_{10}$ is shown on the dehydration curve and is formed by heating the hydrated oxide with water under pressure (Simon, 1923). The pentoxide is acidic and forms salts called **antimonates**.

When a mixture of powdered antimony and potassium nitrate is thrown in portions into a red-hot crucible and the product extracted with warm water, a residue of potassium antimonate remains as a white powder, which dissolves slowly in boiling water. Dilute nitric acid precipitates from the solution a hydrated antimony pentoxide, which forms pure antimony pentoxide on heating gently. A hydrated pentoxide is also formed by the action of hot water on antimony pentachloride, and by oxidising the trioxide in presence of water with chlorine, iodine, or potassium dichromate. With bromine, nitric acid, or a mixture of potassium chlorate and hydrochloric acid, the oxidation of antimony trioxide is incomplete.

Antimony pentoxide is an oxidising agent; when dissolved in cold hydrochloric acid it forms the pentachloride and on adding an iodide the iodine liberated may be titrated: $SbCl_5 + 2KI = SbCl_3 + 2KCl + I_2$.

A solution of potassium antimonate on evaporation forms a gum readily soluble in warm water. The solution gives with sodium salts a white amorphous precipitate (perhaps $2NaSbO_3,7H_2O$) which rapidly forms crystalline **sodium pyroantimonate** $Na_2H_2Sb_2O_7,6H_2O$, sparingly soluble (1 in 350) in cold water and almost insoluble in alcohol. It is one of the least soluble sodium salts. Lithium and ammonium salts are also precipitated. A corresponding potassium salt is formed by oxidising potassium antimonite with permanganate and evaporating the filtrate. Lead antimonate is the pigment *Naples yellow*.

The composition of the alkali antimonates is far from clear. Although formulated above as pyroantimonates, they were called metantimonates by Fremy (1844–8) and Jander (1926) also formulates the sodium salt as $NaSbO_3,3H_2O$. The potassium salt has also been regarded as an orthoantimonate $KH_2SbO_4,2H_2O$, and Pauling (*J.A.C.S.*, 1933, **55**, 1895, 3052) formulated it as $K[Sb(OH)_6]$.

Antimony Sulphides

Antimony trisulphide occurs as *stibnite*. By precipitating a solution of antimony trichloride in dilute hydrochloric acid with hydrogen sulphide, a *red* amorphous sulphide (Klug and Heisig, *J.A.C.S.*, 1939, **61**, 1920), s. g. 4·28, is formed, which if dried at 100° and heated in carbon dioxide at 200° gives off some free sulphur and forms the *greyish-black* rhombic crystalline modification, s. g. 4·65. The red form is used as a pigment (*antimony vermilion*) and in vulcanising rubber, red varieties of which contain it. It is also formed by heating a solution of the trichloride with sodium thiosulphate. If heated at 850° in a stream of nitrogen and the vapour rapidly cooled, lilac-coloured globules of s. g. 4·278 are formed. The red precipitate is insoluble in dilute acids but dissolves in hot concentrated hydrochloric acid (arsenic sulphide is almost insoluble). Colloidal Sb_2S_3 is formed as an orange-red liquid by adding a 0·5 p.c. solution of tartar emetic to hydrogen sulphide water.

Antimony trisulphide is reversibly reduced by heating in hydrogen: $Sb_2S_3 + 3H_2 \rightleftharpoons 2Sb + 3H_2S$. A mixture with nitre and sulphur is used as *blue-fire* in pyrotechny, and in making matches. Sb_2S_3 dissolves in alkali sulphides and hot concentrated solutions of alkalis and alkali carbonates. On dilution, a

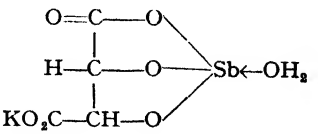
red mixture of Sb_2O_3 and Sb_2S_3 (*kermes mineral*) is precipitated. The solutions and the dark-coloured masses (*livers of antimony*) formed by fusing Sb_2S_3 with alkali sulphides contain **thioantimonites** derived from hypothetical acids H_3SbS_3, $H_2Sb_4S_7$ and $HSbS_2$, and some can be obtained crystalline, *e.g.* pale yellow $Na_3SbS_3,3H_2O$, red $KSbS_2$, red $Na_2Sb_4S_7,2H_2O$. Precipitated Sb_2S_3 is insoluble in warm ammonium carbonate solution (As_2S_3 is soluble).

Antimony pentasulphide Sb_2S_5 is formed as a red precipitate on adding saturated hydrogen sulphide solution to a cold solution of Sb_2O_5 containing 10–20 p.c. of free hydrochloric acid (Bunsen, *Annalen*, 1878, **192**, 305; Bosek, *J.C.S.*, 1895, **67**, 515; Currie, *J. Phys. Chem.*, 1926, **30**, 205). It dissolves in alkalis (even warm ammonia), sodium carbonate (but not ammonium carbonate) and alkali sulphide solutions, forming **thioantimonates**:

$$4Sb_2S_5 + 24KOH = 5K_3SbS_4 + 3K_3SbO_4 + 12H_2O$$
$$Sb_2S_5 + 3Na_2S = 2Na_3SbS_4.$$

Sodium thioantimonate or *Schlippe's salt* (Schlippe, 1821) is formed in large pale yellow tetrahedral crystals $Na_3SbS_4,9H_2O$ by boiling Sb_2S_3 and sulphur with sodium hydroxide solution, filtering and cooling. On acidifying a thioantimonate solution an orange-red precipitate called *golden sulphuret of antimony*, used in vulcanising rubber, is formed. On heating alone or with water or acids it decomposes into sulphur and black Sb_2S_3; it has been regarded as Sb_2S_5 or a mixture of **antimony tetrasulphide** Sb_2S_4 and sulphur (Currie, *loc. cit.*): $2Na_3SbS_4 + 6HCl = Sb_2S_4 + S + 6NaCl + 3H_2S$. The commercial products vary in colour from golden yellow to deep orange, and in composition from Sb_2S_3 almost to Sb_2S_5. The compounds K_3SbS_4 with 3, 5, 6 or $9H_2O$, $(NH_4)_3SbS_4$, $Ba_3(SbS_4)_2,6H_2O$, etc., are known.

Tartar emetic, an important preparation used in medicine and as a mordant, is obtained by boiling antimony oxide with water and cream of tartar (potassium hydrogen tartrate); it is usually formulated (Peligot, 1847) as *potassium antimonyl tartrate* $K(SbO)C_4H_4O_6.\frac{1}{2}H_2O$ containing the *antimonyl* radical —Sb= O, but Reihlen and Hezel (1934) adopt a modification of Schiff's formula (1857):



Bismuth

Metallic bismuth may have been known in antiquity but Agricola says it was unknown to the ancients and describes it in his *Bermannus* (1530) as *bisemutum*; in his *de natura fossilium* (1546) he calls it *plumbum cinereum*. Libavius in his *Commentariorum chymicorum* (1606) mentions it, noting that it was used to soften tin. The name may have been derived from the German *wis mat* (white mass), the modern German name being *Wismuth*. Pott (1739) and

Bergman investigated its compounds. The basic nitrate $Bi(OH)_2NO_3$, discovered by Libavius, is used medicinally in diarrhoea and cholera.

Bismuth occurs *native* with lead, silver and cobalt ores, as the *oxide* Bi_2O_3 *bismite* or *bismuth ochre*, the *sulphide* Bi_2S_3 *bismuthinite* or *bismuth glance*, and the *basic carbonate* $(BiO)_2CO_3$ *bismuthite* or *bismuth spar*. The most important source is Bolivia ; much is extracted from lead ores in Canada and India, and China, Saxony, and Australia are noteworthy sources.

The metal is obtained from native bismuth by liquation, viz. heating in sloping iron tubes when the fusible bismuth (m.p. 271°) flows away. Oxide and carbonate ores are dissolved in hydrochloric acid and the solution of $BiCl_3$ either poured into water to precipitate BiOCl or reduced to bismuth by iron. Sulphide ores are roasted and the oxide reduced by carbon, iron, and a flux ; the temperature is kept fairly low as the oxide is volatile. Flue dusts from lead, copper and tin ores, and anode slimes from copper and lead refining, are worked for bismuth. The metal is refined by electrolysis in bismuth chloride and hydrochloric acid in a similar way to copper (p. 328). Very pure bismuth is made by recrystallising the nitrate from a solution containing a large excess of concentrated nitric acid, heating the nitrate to form the oxide, and reducing this by heating with potassium cyanide. Refined commercial bismuth is 99·0 to 99·9 p.c. pure and for making pharmaceutical products must be free from lead and arsenic. *Precipitated bismuth* is a dull grey powder formed by reducing a solution of $BiCl_3$ in hydrochloric acid by hypophosphorous acid, and a colloidal solution can be obtained.

Bismuth is reddish-white, s. g. 9·80, brittle and easily powdered, and is a poor conductor of heat and electricity. It is strongly diamagnetic. Large obtuse rhombohedra resembling cubes, usually covered with a superficial film of oxide showing iridescent colours, are formed when the fused metal is cooled. A trace of tellurium alters the appearance and properties of bismuth. Bismuth and its alloys with other metals, which have very low melting points, expand on solidification, and the alloys are used as stereometal in printing.

Wood's fusible metal (m.p. 71°) contains 4 bismuth + 2 lead + 1 tin + 1 cadmium, **Rose's metal** (m.p. 93·75°) 2 bismuth + 1 lead + 1 tin, and **Lipowitz' alloy** (m.p. 60°–65°) 15 bismuth + 8 lead + 4 tin + 3 cadmium. Alloys of lead, bismuth and tin, melting slightly above 100°, are used in the construction of automatic sprinklers ; when the fusible metal plug is melted water is discharged over the fire. Less fusible alloys are used as safety plugs in boilers.

Bismuth boils at 1450° giving a green vapour, the density of which between 1600° and 1700° indicates partial dissociation : $Bi_2 \rightleftharpoons 2Bi$, which is complete at 2000°. It volatilises appreciably at lower temperatures (at 292° in vacuum). The metal is unchanged in dry air and is slowly attacked by water only in presence of oxygen. When fused it slowly oxidises in air, and when strongly heated burns with a bluish-white flame, forming brown fumes of Bi_2O_3. Pyrophoric bismuth is formed on heating the mellitate under reduced pressure. Bismuth decomposes steam slowly when strongly heated, liberating hydrogen.

It does not dissolve in dilute sulphuric or hydrochloric acid in absence of oxygen, but nitric acid dissolves it forming the nitrate $Bi(NO_3)_3$. It readily dissolves in aqua regia, forming the chloride $BiCl_3$. Boiling concentrated sulphuric acid converts it into the sulphate $Bi_2(SO_4)_3$, sulphur dioxide being evolved.

Bismuth Compounds

Bismuth is more electropositive than the other elements in its group, and its chemical properties are intermediate between those of lead and antimony. The chloride $BiCl_3$, although easily fusible and volatile and soluble in organic solvents, is an electrolyte when fused, and stable oxysalts such as the nitrate, sulphate and basic carbonate are known. Many salts with organic acids are soluble in benzene. There is a marked tendency to form basic salts, usually formulated as containing the univalent *bismuthyl radical*—Bi=O. These (unlike the antimonyl compounds) are insoluble in tartaric acid. Unlike antimony, bismuth has little tendency to show a higher valency, all the stable compounds being of tervalent bismuth, although higher oxides contain 4, 5 or possibly 6-valent bismuth. The so-called *bismuthous compounds*, supposed to contain bivalent bismuth, are now regarded as mixtures or solid solutions of metal and tervalent compounds, although the phase diagram method used is not quite decisive, as the compounds might be decomposed at higher temperatures.

Bismuth hydride.—As the stability of the hydrides in the sub-group decreases from nitrogen to antimony, bismuth hydride would be expected to be very unstable. When the hydrogen evolved by the action of 4*N* sulphuric or hydrochloric acid on an alloy of equal parts of bismuth and magnesium is passed through a heated tube, it deposits a brown mirror of bismuth in front of the heated spot and a fainter one behind, suggesting that a trace of a gaseous hydride (BiH_3?), which is very unstable, is formed. It is absorbed to some extent by water and is more soluble in dilute alkali, indicating that it is acidic rather than basic; the basic character decreases from ammonia to stibine earlier in the group. Thorium-C, an isotope of bismuth, when deposited on magnesium, gives a radioactive gaseous hydride on solution in acid (Paneth, etc., 1918–20).

Bismuth Halides

BiF_3, white or grey cubic crystals, m.p. 800°.

$BiCl_3$, white crystals, m.p. 232·5°, b.p. 447°.

$BiBr_3$, yellow crystals, m.p. 215°, b.p. 453°.

BiI_3, red-brown or black hexagonal crystals, m.p. 412°.

All these halides are formed by the action of halogens on the metal; fluorine does not react easily even at a red heat, and the other halogens react without incandescence on heating. Bismuth fluoride is stable to water but the other halides form basic salts.

Bismuth fluoride BiF_3 is formed as a white powder, non-volatile at a red heat, on evaporating a solution of bismuth trioxide in hydrofluoric acid. With excess of oxide an **oxyfluoride** BiOF is formed.

Compounds of 5-valent bismuth are the double salt $K[BiOF_4]$ or $BiOF_3,KF$ (Ruff, 1908), and the white **pentafluoride** BiF_5 (sublimes at 550°), formed from BiF_3 and fluorine (von Wartenberg, 1940).

Bismuth chloride $BiCl_3$ is a soft white crystalline substance formed on passing excess of chlorine over bismuth ; by heating bismuth with mercuric chloride (Boyle, 1663) : $2Bi + 3HgCl_2 = 2BiCl_3 + 3Hg$; or by dissolving bismuth in aqua regia, evaporating, and distilling the crystals of $BiCl_3,2H_2O$ deposited. The vapour density of bismuth chloride corresponds with $BiCl_3$. The solution in concentrated hydrochloric acid contains **chlorobismuthous acid** ; at 0° crystals of $H[Bi_2Cl_7],3H_2O$ deposit, stable at room temperature. Salts of $HBiCl_4$, H_2BiCl_5 and HBi_2Cl_7 are known. The compounds $BiCl_3,NO$ and $BiCl_3,NOCl$ are known.

A solution of bismuth chloride when poured into water gives a white precipitate of **bismuth oxychloride** BiOCl, which can be obtained crystalline. It is also deposited when bismuth nitrate solution is added to sodium chloride solution. It resembles silver chloride in turning grey and losing chlorine when exposed to light.

A supposed black **dichloride** $BiCl_2$, formed on heating the trichloride with excess of bismuth, or bismuth with mercurous chloride at 250°, is probably a solid solution of bismuth in bismuth trichloride (Marino and Becarelli, 1915–16).

Bismuth perchlorate $Bi(ClO_4)_3,5H_2O$ forms a clear solution even with hot water, as the basic salts $BiOClO_4$ and $Bi(OH)_2ClO_4$ are soluble.

Bismuth bromide $BiBr_3$ is formed from the elements in golden-yellow crystals, decomposed by water into the white **oxybromide** BiOBr. **Bismuth iodide** BiI_3 is a black powder formed by adding bismuth trioxide to a solution of iodine in stannous chloride solution saturated with hydrogen chloride. It is only slowly decomposed by water into the red **oxyiodide** BiOI, which is precipitated by alkali iodide from a faintly acid solution of a bismuth salt. Bismuth iodide dissolves in hydriodic acid forming **iodobismuthous acid** $HBiI_4,4H_2O$, and in alkali iodides forming red crystalline salts, *e.g.* $KBiI_4$.

Bismuth Oxides

The only well-defined oxide is the stable **bismuth trioxide** Bi_2O_3. Rather indefinite higher oxides, possibly Bi_2O_4, Bi_2O_5 and Bi_2O_6 are known, but the supposed black dioxide Bi_2O_2 is shown by its magnetic susceptibility to be a mixture of Bi_2O_3 and finely divided bismuth (Neusser, 1924).

The " dioxide " is formed as a black precipitate on adding a bismuth salt to sodium stannite solution (stannous chloride solution added to excess of sodium hydroxide solution), often with a white precipitate of bismuth hydroxide, hence this is called the " magpie test " for bismuth.

Bismuth trioxide Bi_2O_3 (rhombic) is a pale yellow powder (greenish-grey when not quite pure) which darkens on heating. It is obtained by heating the metal, hydroxide, basic carbonate or nitrate to redness in air. It melts at a red heat and solidifies at 820° ; at 704° the solid changes into a second rhombic form ; a supposed third form of higher m.p., obtained in yellow needles on heating in

a porcelain crucible to the m.p., probably contains silica. Bismuth oxide is easily reduced by heating with carbon. It is used to make some optical glasses and an iridescent white glaze on porcelain, and mixed with gold in gilding porcelain ; a mixture of Bi_2O_3 and Cr_2O_3 fused on glass gives a lemon-yellow colour.

Bismuth hydroxide $Bi(OH)_3$ is formed as a white gelatinous precipitate, which becomes crystalline, on adding alkali or ammonia to a solution of a bismuth salt, preferably the nitrate, or (free from oxysalts) by precipitating from an alkaline solution by acid. It is insoluble in excess of alkali unless shaken with *concentrated* sodium hydroxide solution (Knox, *J.C.S.*, 1909, **95**, 1760) or unless glycerol is added. It is readily soluble in acids. At 100° it is said to form BiO(OH), and at a red heat it gives Bi_2O_3. The X-ray diffraction pattern of bismuth hydroxide is different from that of Bi_2O_3, but it is not certain if the compound is $Bi(OH)_3$ or BiO(OH).

Higher oxides of bismuth are precipitated as reddish-brown powders by adding oxidising agents to alkaline suspensions of bismuth trioxide. In hot dilute alkali, chlorine precipitates a scarlet powder, principally **bismuth tetroxide** Bi_2O_4 ; in concentrated alkali some **bismuth pentoxide** Bi_2O_5 is also precipitated. Both oxides dissolve in hot nitric acid of s. g. 1·2 with evolution of oxygen. By oxidising with ferricyanide or persulphate in concentrated alkali, a small amount of pale brown **bismuth hexoxide** Bi_2O_6, insoluble in nitric acid, is formed (Worsley and Robertson, *J.C.S.*, 1920, **117**, 63 ; cf. Deichler, *Z. anorg. Chem.*, 1899, **20**, 81 (bibl.) ; Zintl and Rauch, *ibid.*, 1924, **139**, 397).

The higher oxides lose oxygen on heating and are reduced by warm concentrated hydrochloric or sulphuric acids :

$$Bi_2O_4 + 8HCl = 2BiCl_3 + 4H_2O + Cl_2$$
$$Bi_2O_5 + 3H_2SO_4 = Bi_2(SO_4)_3 + 3H_2O + O_2.$$

The higher oxides of bismuth show *acidic* properties. On fusing bismuth trioxide with potassium hydroxide in air a brown mass of **potassium bismuthate**, perhaps $KBiO_3$, is formed ; it is hydrolysed by water and hydrated Bi_2O_5 precipitated. Potassium bismuthate is used as an oxidising agent ; with *cold* solutions of manganous salts in dilute nitric acid it forms permanganic acid. In its higher oxides bismuth shows a resemblance to lead.

Basic bismuth carbonate $(BiO)_2CO_3,\frac{1}{2}H_2O$ precipitates as a white powder on adding ammonium carbonate solution to bismuth nitrate solution. It loses water at 100° and carbon dioxide at higher temperatures. It is given as a " bismuth meal " before X-radiology of the digestive tract, as it is opaque to X-rays.

Bismuth nitrate is obtained in deliquescent triclinic crystals $Bi(NO_3)_3,5H_2O$ by evaporating a solution of bismuth or the oxide or basic carbonate in warm 20 p.c. nitric acid : $2Bi + 8HNO_3 = 2Bi(NO_3)_3 + 2NO + 4H_2O$. A solution in dilute nitric acid when poured into a large volume of water deposits a white crystalline powder of the **basic nitrate** (*subnitrate*) $Bi(OH)_2NO_3$, used in medicine and formerly as a cosmetic (" flake white "). On washing with water this gradually forms $(BiO)_2(OH)NO_3$, unchanged by boiling water. The commercial basic nitrate is a definite compound $6Bi_2O_3,5N_2O_5,8\frac{1}{2}H_2O$. Anhydrous

$Bi(NO_3)_3$ cannot be obtained by heating the crystal hydrate, and on drying this over P_2O_5 in vacuum the hydrate $Bi(NO_3)_3,1\frac{1}{2}H_2O$ is obtained unless the drying is prolonged for a year, when anhydrous $Bi(NO_3)_3$ remains (Picon, 1925).

By grinding bismuth nitrate crystals with mannitol and adding water a clear solution is formed; the pure salt gives a clear solution in dilute nitric acid.

Bismuth sulphide Bi_2S_3 is formed in lead-grey rhombic crystals by fusing bismuth with sulphur, and as a brownish-black precipitate when hydrogen sulphide is passed into a solution of a bismuth salt (solubility 0·2 mg./lit.). The precipitate dissolves in dilute nitric acid (with separation of sulphur) and in boiling concentrated hydrochloric acid, but not in alkalis or ammonium sulphide, since (unlike sulphides of arsenic, antimony and tin) it does not form thio-salts in this way.

Thio-salts of bismuth are formed by dissolving the precipitated sulphide in concentrated *potassium* sulphide solution or by fusion with alkali sulphides; $KBiS_2$ and $NaBiS_2$ form fine crystals with a metallic lustre, rapidly oxidised in air. On diluting a solution of the sodium salt, Bi_2S_3 is precipitated, and Bi_2S_3 is only sparingly soluble in sodium sulphide solution.

Bismuth sulphite $Bi_2(SO_3)_3$ is a white crystalline powder used medicinally, formed by the action of sulphurous acid on the basic carbonate or from solutions of bismuth nitrate and sodium sulphite.

Bismuth sulphate $Bi_2(SO_4)_3$ is a white amorphous solid obtained by evaporating the metal with concentrated sulphuric acid. With water it forms a sparingly soluble basic sulphate $Bi_2(OH)_4SO_4$, which on heating forms yellow bismuthyl sulphate $(BiO)_2SO_4$. With potassium sulphate a salt $KBi(SO_4)_2$ is formed.

Sodium thiosulphate with a solution of a bismuth salt gives a clear solution containing **sodium bismuth thiosulphate** $Na_3[Bi(S_2O_3)_3]$, which does not react with iodine. The solution quickly decomposes and deposits bismuth sulphide. It gives with potassium salts a sparingly soluble yellow **potassium bismuth thiosulphate** $K_3[Bi(S_2O_3)_3],\frac{1}{2}H_2O$, and the reaction may be used in the detection of potassium. On boiling sodium bismuth thiosulphate solution the bismuth is quantitatively precipitated as sulphide: $2Bi''' + 3S_2O_3'' + 3H_2O = Bi_2S_3 + 3H_2SO_4$.

Many salts of bismuth with organic acids (salicylate, basic gallate, basic dibromohydroxynaphthoate, hydroxyiodogallate, etc.) and phenols (β-naphthol, pyrogallol, etc.) are used in pharmacy.

Vanadium

In 1801 Del Rio discovered in a Mexican lead ore a new element which gave coloured salts with acids, but Descotils in 1804 reported that the mineral was lead chromate. Sefström in 1830 discovered in Swedish iron and slags an element which was called *vanadium* (after the Scandinavian goddess Vanadis), and Wöhler showed that the Mexican ore is lead vanadate. Berzelius, with a few grams of Sefström's material, prepared a number of compounds of vanadium, which he supposed formed an acidic oxide VO_3 like CrO_3. In 1867 Roscoe found that the oxide was V_2O_5, and first prepared the metal, what Berzelius had regarded as vanadium being the oxide V_2O_3 or the nitride VN.

Vanadium is widely distributed, the principal ores being *carnotite* or potassium uranyl vanadate $K_2(UO_2)(VO_4)_2,3H_2O$, *vanadinite* $3Pb_3(VO_4)_2,PbCl_2$ (p. 236), and especially the impure sulphide *patronite* found at 17,000 ft. on the Peruvian Andes and in North Rhodesia. Vanadium is found in small amounts in clays, rocks, coal and crude oil (Alexander, *J.S.C.I.*, 1929, **48**, 871, 895R.).

Ferro-vanadium is made from patronite and used in making steel of high tensile strength (Saklatvalla, *Trans. Amer. Electrochem. Soc.*, 1920, **37**, 341). Pure vanadium is very difficult to obtain, as it readily combines with oxygen, carbon and nitrogen ; it is made by heating V_2O_5, calcium and calcium chloride in a steel bomb at 900°–950° (Marden and Rich, *Ind. Eng. Chem.*, 1927, **19**, 786) : $V_2O_5 + 5Ca + 5CaCl_2 = 2V + 5(CaO,CaCl_2)$, and when so prepared is soft and ductile.

Vanadium has chemical analogies with nitrogen and arsenic ; it forms compounds and corresponding oxides in which it has valencies of 2, 3, 4 and 5, and is a transitional element (p. 261) :

(i) *Hypovanadous compounds*, V_2O_2 and VX_2, containing V^{II}.
(ii) *Vanadous compounds*, V_2O_3 and VX_3, containing V^{III}.
(iii) *Hypovanadic compounds*, V_2O_4 or VO_2 and VX_4, containing V^{IV}, but readily forming *vanadyl compounds* containing the bivalent radical $V^{IV}O$, viz. VOX_2.
(iv) *Vanadic compounds* VX_5, and *vanadates* derived from the acidic oxide V_2O_5, all containing V^{V}.

The compounds of bivalent vanadium are definite and show analogies with those of other 2-valent transitional elements : $VSO_4,7H_2O$ is isomorphous with $FeSO_4,7H_2O$ and forms mixed crystals with $MgSO_4,7H_2O$ and $CrSO_4,7H_2O$; and $(NH_2)_2[V^{II}(SO_4)_2],6H_2O$, like $(NH_4)_2[Fe(SO_4)_2],6H_2O$, is less easily oxidised than the sulphate. Noteworthy are the complex cyanides $K_4[V^{II}(CN)_6]$ and $K_3[V^{III}(CN)_6]$, analogous to ferro- and ferricyanides. (Definite compounds of 2-valent Nb and Ta are restricted to complex halide acids (p. 646)).

The common oxide is the reddish-yellow sparingly soluble **pentoxide** V_2O_5, which dissolves in concentrated sulphuric acid and on dilution a pale yellow solution is formed. Sulphur dioxide reduces this to a blue solution of **vanadyl sulphate** $(V^{IV}O)SO_4$. Magnesium and hydrochloric acid reduce it to a green solution of **vanadium trichloride** $V^{III}Cl_3$, and by the prolonged action of zinc and dilute sulphuric acid (more rapidly with zinc amalgam) a lavender solution of **hypovanadous sulphate** $V^{II}SO_4$ is formed. The vanadous and hypovanadous compounds are very powerful reducing agents.

A general view of some vanadium compounds corresponding with the different valencies is given below ; except VCl_4 and $VOCl_3$ they are all solids.

VII	VIII	VIV	VV
VCl_3 apple-green	VF_3 greenish-yellow	VF_4 brown	VF_5 white
VO black	VCl_3 peach-blossom	VOF_2 yellow	VOF_3 pale yellow
VS black	$[V(NH_3)_6]Cl_3$ brown	VCl_4 cherry-red liquid, b.p. 153°	$VOCl_3$ lemon-yellow liq., b.p. 127°
$VSO_4,7H_2O$ violet	VOCl brown	$VOCl_2$ green	V_2O_5 and vanadates red or orange
$K_4[V(CN)_6],3H_2O$ brownish-yellow	$V(OH)_3$ grey-green	VO_2 indigo-blue	V_2S_5 black
	V_2O_3 black	$(VO)SO_4$ grey and blue	
	V_2S_3 black		
	$V_2(SO_4)_3$ forms alums $M^{IVIII}(SO_4)_2,12H_2O$		
	VN grey-brown		
	$K_3[V(CN)_6]$		

The oxides VO_2 (easily soluble in acids and alkalis) and V_2O_3 (insoluble in most acids) are formed by heating V_2O_5 in hydrogen, and VO by heating V_2O_5 with potassium; VO dissolves in acids without evolution of hydrogen to form V^{II} salts. Salts corresponding with ortho-, pyro- and metavanadic acids H_3VO_4, $H_4V_2O_7$ and HVO_3 are known; sodium orthovanadate $Na_3VO_4,12H_2O$ is isomorphous with $Na_3PO_4,12H_2O$.

Vanadic acid forms *polyvanadates* containing polymerised anions, *e.g.* V_6O_{17}'''' from $H_4V_6O_{17}$ or $3V_2O_5,2H_2O$, in acid solution. With niobium and tantalum such salts are formed by heating the pentoxides with bases, the commonest type being $4M_2^IO,3(Nb,Ta)_2O_5$. Vanadic acid forms a number of complex *heteropoly acids* (p. 757) with other acids (phosphoric, arsenic, silicic, oxalic, molybdic, tungstic, and sometimes two of these), whilst (apart from oxalic acid compounds) niobium and tantalum show little tendency to form such acids.

A solution of V_2O_5 in dilute sulphuric acid gives with hydrogen peroxide a red colour, usually supposed to be due to *pervanadic acid* HVO_4, insoluble in ether. It may contain $[V^V(O_2)]_2(SO_4)_3$, hydrolysed by dilution into yellow $V(O_2)(OH)_3$ (Meyer, *Z. anorg. Chem.*, 1927, **161**, 321). The perniobic and pertantalic acids are more stable, the last being stable at 100°.

The oxide VO_2 is amphoteric and many compounds of the *vanadyl* radical $VO^{\cdot\cdot}$ are known; NbO_2 and TaO_2 do not form salts.

The *pentafluoride* VF_5 is formed by heating VF_4 in a current of nitrogen, when it sublimes and leaves VF_3: $2VF_4 = VF_5 + VF_3$. VF_4 is formed by the action of anhydrous hydrofluoric acid on VCl_4. There is no pentachloride. On passing chlorine over a heated mixture of V_2O_5 and carbon or HCl gas over heated V_2O_5, the lemon-yellow mobile liquid *oxytrichloride* $VOCl_3$ is formed. This is not decomposed on boiling with sodium or potassium. By passing the vapour of $VOCl_3$ and chlorine over heated carbon, or chlorine over heated vanadium or the nitride VN, the dark cherry-red viscous liquid *tetrachloride* VCl_4 is formed; by passing VCl_4 vapour and hydrogen through a red-hot tube a peach-blossom coloured sublimate of the *trichloride* VCl_3 is formed. On heating VCl_3 to redness in nitrogen an apple-green residue of the *dichloride* VCl_2 remains: $2VCl_3 = VCl_4 + VCl_2$. The trichloride is formed by heating $VOCl_3$ with sulphur: $2VOCl_3 + S = SO_2 + 2VCl_3$ (Bodforss, *Z. anorg. Chem.*, 1935, **221**, 382).

Vanadous sulphate $V_2^{III}(SO_4)_3$ forms violet or ruby-red alums with sulphates of alkali metals and thallium.

Vanadium pentoxide is used as a catalyst in the oxidation of naphthalene vapour and air to phthalic anhydride, and of sulphur dioxide and air to sulphur trioxide, and vanadium compounds (which are poisonous) are used in making ink, in dyeing, as drying accelerators in paints and varnishes, as insecticides, in photography and medicine, and in glass manufacture.

Niobium and Tantalum

Niobium and tantalum until recently were very rare; niobium (formerly, and still often, called *columbium*) was discovered in a mineral from Connecticut by Hatchett in 1801, and tantalum (so called from Tantalus, because "when placed in acids it is incapable of taking them up") by Ekeberg in 1802 in some minerals in Finland. The chief minerals are *columbite* and *tantalite*, both $Fe(Nb,Ta)O_3$, the first richer in niobium and the second in tantalum. The metals are now extracted from American minerals and are finding many uses

(Balke, *Ind. Eng. Chem.*, 1929, **21**, 1002 ; 1935, **27**, 1166). Tantalum, density 16·6, m.p. 2850°, is ductile and is used in radio-valve grids and plates ; and niobium, density 8·56, m.p. 1950°, for chemical apparatus instead of platinum, since the metals are acid-resisting. Niobium improves stainless steel and the carbides of the two elements, which are very hard, are used for cutting tools. The metals oxidise in air at a red heat and are disintegrated by fused alkalis.

Niobium and tantalum form white solid acidic typical *pentoxides* Nb_2O_5 and Ta_2O_5, but the salts of these are mostly complex. The elements show valencies of 2, 3, 4 and 5.

Valency : II	III	IV	V
NbO?	$NbCl_3$	NbO_2	NbF_5 Nb_2O_5 } and salts
$H[Nb_3^{II}Cl_7(H_2O)],3H_2O$	Nb_2O_3	TaO_2	TaF_5 Ta_2O_5 }
	$TaCl_3$	TaS_2	$NbOF_3$
$H[Ta_3^{II}Cl_7(H_2O],3H_2O$	$TaBr_3$		$NbCl_5$
			$TaCl_5$
			$NbOCl_3$
			$NbBr_5$
			$TaBr_5$
			$TaOBr_3$
			TaI_5

The complex fluorides, the sparingly soluble *fluotantalate* K_2TaF_7 (in the ion TaF_7'' the tantalum has a coordination number of 7), and the easily soluble *fluoxyniobate* K_2NbOF_5,H_2O, are used in the separation of the elements. By crystallising NaF and NbF_5 from *anhydrous* hydrofluoric acid the salts $NaNbF_6$ and Na_2NbF_7 are formed (Laubengayer and Polzer, *J.A.C.S.*, 1941, **63**, 3264).

Protoactinium

The steady decrease in acidic character in the series V_2O_5, Nb_2O_5 and Ta_2O_5 reaches a climax in *protoactinium pentoxide*, a heavy white powder Pa_2O_5, which is basic and resembles thorium dioxide ThO_2 rather than the other oxides : it is soluble in concentrated sulphuric acid and insoluble in fused alkali. The compounds of the radioelement protoactinium (or protactinium) were separated in fairly large amounts ($\frac{1}{2}$ g. or more) from pitchblende residues by von Grosse (*Ind. Eng. Chem.*, 1935, **27**, 422). The metal, formed by electron bombardment of Pa_2O_5 on a copper target, is stable in air. The chloride $PaCl_5$ forms colourless volatile needles.

CHAPTER XXII

OXYGEN AND OZONE

GROUP VI of the Periodic System comprises nine elements (apart from radio-elements).

Sub-Group (*a*) (Even Series)

	Cr	Mo	W	U
Atomic number - -	24	42	74	92
Electron configuration -	2·8·13·1	2·8·18·13·1	2·8·18·32·12·2	2·8·18·32·18·12·2
Density - - -	7·14	10·2	19·3	18·69
Atomic volume - -	7·28	9·42	9·54	12·74
Melting point - -	1800°	2620°	3390°	1689°
Boiling point - -	2200°	3700°	5900°	3500° ?

Sub-Group (*b*) (Odd Series)

	O	S	Se	Te
Atomic number - -	8	16	34	52
Electron configuration -	2·6	2·8·6	2·8·18·6	2·8·18·18·6
Density (solid) - -	1·4256	2·1	4·8	6·235
Atomic volume - -	11·2	15·3	16·5	20·4
Melting point - -	−218·4°	112·8°	220·2°	452·5°
Boiling point - -	−183°	444·60°	684·8°	1390°

The marked difference between the two sub-groups as contrasted with Groups II–V is reminiscent of Group I and is accentuated in Group VII (halogens, Mn and Re) and VIII (inert gases, platinum metals).

The elements of Sub-group *b* are classed as non-metals, but there is a steady increase in electropositive character with increasing atomic weight; tellurium has the physical properties of a brittle metal such as antimony and can be called a metalloid (p. 536). The elements of Sub-group *a* are all metals. The m.ps. and b.ps. rise in both sub-groups with increasing atomic weight, except in the case of uranium, and the atomic volumes all increase. The elements of Sub-group *b* form molecules containing more than one atom in the vapour state.

Except in the case of oxygen, the maximum valency of all the elements is 6, but lower valencies of 2 (completing the inert gas shell) and 4 are shown in Sub-group *b*, and of 2, 3, 4, 5 and 6 in Sub-group *a*, the metals of which are markedly transitional elements. They show close resemblances to neighbouring elements (V, Mn, Fe, Co, Ni) and have varying valencies, electrons in the shell below the valency electrons (which also contains a complete group of 8 electrons) functioning easily as valency electrons:

Cr	2 | 8 | 2 . 6 . 5 | 1
Mo	2 | 8 | 18 | 2 . 6 . 5 | 1
W	2 | 8 | 18 | 32 | 2 . 6 . 4 | 2
U	2 | 8 | 18 | 32 | 18 | 2 . 6 . 4 | 2

Because of their transitional character these elements form strongly-coloured compounds which are often paramagnetic. The *M* and *N* electrons next to the outer shell are easily lost or function as valency electrons, Cr forming $Cr^{\cdots}$ and CrO_4'' (derived from Cr^{6+}), and the other elements forming compounds up to the valency of 6. In these, the electrons lost or shared include 5 from the inner *M* or *N* group for Cr and Mo, and 4 from the *O* or *P* group for W and U. The elements of Sub-group *b* are predominatingly electronegative, even tellurium combining with many metals to form tellurides and forming acidic oxides. The elements of Sub-group *b* all form gaseous *hydrides* RH_2, the stability decreasing from O to Te, whilst the acidity increases; those of Sub-group *a* do not form hydrides (except possibly chromium, which is said to form a non-volatile CrH_6). The elements of both sub-groups (except oxygen) form typical acidic *trioxides* RO_3 in which R is 6-valent, and salts M_2RO_4 of the acids H_2RO_4, which are also sometimes known; the common telluric acid is H_6TeO_6, and in Sub-group *a* these acids are often more complex, the tendency to form complex polyacids increasing from chromium to tungsten.

For the same element the acidic character of the hydroxide increases with the valency, *e.g.* $Cr^{II}(OH)_2$ and $Cr^{III}(OH)_3$ are basic, $Cr^{VI}O_4H_2$ or $Cr^{VI}O(OH)_2$ is acidic; this may be due to the increasing tendency of the nuclear charge to bind oxygen and repel protons. The decreasing acidity with increasing atomic weight may be the result of increasing atomic volume, the action of the nuclear charge being weakened.

In Sub-group *b* the dioxides RO_2 are also acidic, forming salts M_2RO_3. The lower oxides of Sub-group *a* are more basic and other oxides *e.g.* R_2O_3 related to those of neighbouring transitional elements are known.

The *halides* are predominantly covalent and volatile, although those of lower valencies of Sub-group *b* are either ionic or associated into peculiar groupings. Those of Sub-group *b* are hydrolysed by water or alkalis (Cl_2O and Cl_2O_7 are acidic anhydrides and ClO_2—not hydrolysed by water—and Cl_2O_6 are mixed anhydrides), and some of those of Sub-group *a* are also hydrolysed. All the elements (except oxygen) form stable *oxychlorides* $R^{VI}O_2Cl_2$ which are volatile covalent compounds.

Oxygen

The discovery of oxygen and the recognition of the part it plays in combustion, the calcination of metals, and respiration, marked a turning-point in the history of Chemistry and the beginning of the modern period. Hooke (*Micrographia*, 1665) had recognised that only part of the atmosphere is concerned in combustion and probably exists in a combined form in nitre, and Mayow (*Tractatus quinque*, 1674) made further experiments on combustion and recognised the participation of the active part of the air in respiration. Hooke called this part of the air and nitre *nitrous air* and Mayow *nitro-aerial spirit*. Oxygen gas was first isolated about 1772 by Scheele (*On Air and Fire*, 1777) by heating nitre and some metallic oxides, including mercuric oxide. It was independently obtained by Priestley in 1774 by heating mercuric oxide. Scheele called the gas *fire air* and Priestley *dephlogisticated air*. The elementary nature of oxygen was

first clearly recognised by Lavoisier in 1775–7 and he called it *principe oxygine* (Greek *oxus*, sour) because he thought it was an essential constituent of acids.

Free oxygen O_2 occurs in the atmosphere (21 p.c. by vol. or 23 p.c. by wt.) and takes part in combustion and respiration. It is sparingly soluble in water but the small quantity dissolved in river and sea waters is essential to the life of fish. Its solubility in sea water is about 0·78 that in pure water. Combined oxygen occurs in water, vegetable and animal tissues, rocks and in many minerals; it occurs to a larger extent (about 50 p.c.) in the earth's crust than any other element (p. 3).

There are three *isotopes* of oxygen (Giauque and Johnston, 1929) with the approximate abundance ratios $^{16}O : {}^{17}O : {}^{18}O = 99{\cdot}76 : 0{\cdot}04 : 0{\cdot}20$, atmospheric oxygen being about 7 p.p.m. heavier than water oxygen (Dole, *J.A.C.S.*, 1935, **57**, 2731).

Preparation of oxygen.—Oxygen is evolved on heating the *oxides* of mercury, silver, gold and platinum. *Mercuric oxide* decomposes at about 450° and the reaction is reversible: $2HgO \rightleftharpoons 2Hg + O_2$. This was the basis of Lavoisier's well-known experiment. *Silver oxide*, precipitated from silver nitrate solution by alkali hydroxide in absence of carbon dioxide, gives pure oxygen at about 350°: $2Ag_2O = 4Ag + O_2$.

Hydrogen peroxide and the *dioxides* of barium, lead and manganese decompose on heating into lower oxides and oxygen:

$$2H_2O_2 = 2H_2O + O_2 \qquad 2BaO_2 \rightleftharpoons 2BaO + O_2$$
$$2PbO_2 \rightleftharpoons 2PbO + O_2 \qquad 3MnO_2 = Mn_3O_4 + O_2 \text{ (bright red heat)}$$

The absorption of atmospheric oxygen by heated barium oxide and the evolution of oxygen from the barium peroxide on reducing the pressure (p. 126) was the basis of the *Brin process* (Boussingault, 1852; Brin, 1879), formerly used for the technical preparation of oxygen.

Oxygen is evolved when water is dropped on *sodium peroxide* (explosion may result if this contains metallic sodium): $2Na_2O_2 + 2H_2O = 4NaOH + O_2$.

Manganese dioxide evolves oxygen when heated with concentrated sulphuric acid: $2MnO_2 + 2H_2SO_4 = 2MnSO_4 + 2H_2O + O_2$.

Oxygen may be obtained from *water* by electrolysis; pure oxygen is evolved at the anode in the electrolysis of barium hydroxide solution; it is passed over red-hot platinum to remove traces of hydrogen and dried with pure phosphorus pentoxide (Burt and Edgar, *Phil. Trans.*, 1916, **216**, 393). On prolonged electrolysis an explosive mixture of hydrogen and oxygen may be evolved from the anode (Stoddart, *Proc. Roy. Soc.*, 1935, **152**, 273): $2OH = H_2 + O_2$.

Oxygen is set free on exposing chlorine water in an inverted flask to sunlight (Berthollet, 1785), and by passing a mixture of steam and chlorine through a red-hot porcelain or silica tube (Gay-Lussac and Thenard, 1811): $2H_2O + 2Cl_2 = 4HCl + O_2$.

Some *salts rich in oxygen* (chlorates, perchlorates, bromates, iodates, periodates, nitrates, persulphates, dichromates and permanganates) evolve oxygen on heating.

Potassium nitrate requires a fairly high temperature in a hard glass tube :

$$2KNO_3 = 2KNO_2 + O_2.$$

Potassium chlorate melts at 357° and at 380° begins to evolve oxygen (Berthollet, 1786) :

$$(1)\quad 2KClO_3 = 2KCl + 3O_2.$$

As the reaction proceeds the evolution of gas slackens and the mass becomes pasty from formation of perchlorate (m.p. 610°) :

$$(2)\quad 4KClO_3 = 3KClO_4 + KCl.$$

On raising the temperature the perchlorate melts and evolves oxygen : finally solid potassium chloride (m.p. 800°) remains :

$$(3)\quad KClO_4 = KCl + 2O_2.$$

Some chlorate is formed as an intermediate stage in the decomposition of the perchlorate. Reactions (1) and (2) proceed simultaneously and *independently* from the beginning (Frankland and Dingwall, *J.C.S.*, 1887, **51**, 274 ; Teed, *ibid.*, 283 ; Scobai, *Z. phys. Chem.*, 1903, **44**, 319 ; Otto and Fry, *J.A.C.S.*, 1924, **125**, 82 ; Blau and Weingand, *Z. Elektrochem.*, 1921, **27**, 1). The equation :

$$2KClO_3 = KCl + KClO_4 + O_2,$$

due to Graham, but shown to be incorrect by Marignac (1843) was, according to Sodeau (*J.C.S.*, 1902, **81**, 1066), "at last disappearing from text-books," although it still frequently makes its appearance. According to Stas, the oxygen evolved at high temperatures contains a little chlorine, but Fowler and Grant (*J.C.S.*, 1890, **57**, 272) and Otto and Fry say this is not present in the first portion of gas from *pure* chlorate.

Potassium permanganate at 240° evolves pure oxygen and leaves a black powder of a mixture of potassium manganate and manganese dioxide (Thenard, 1856) : $2KMnO_4 = K_2MnO_4 + MnO_2 + O_2$. This is a good method for preparing pure oxygen. On adding a little water to the cooled residue a green solution of manganate is formed.

A solution or paste of *bleaching powder* when heated with a few drops of cobalt chloride solution rapidly evolves oxygen (Mitscherlich, 1843) : $Ca(OCl)_2 = CaCl_2 + O_2$. A black cobalt peroxide CoO_2 (or Co_4O_7 or CoO_3) is precipitated and acts as a catalyst (p. 142), probably being alternately reduced and oxidised.

Chromium trioxide and *potassium dichromate* evolve oxygen when heated with concentrated sulphuric acid (Balmain, 1842) :

$$4CrO_3 + 6H_2SO_4 = 2Cr_2(SO_4)_3 + 6H_2O + 3O_2$$
$$2K_2Cr_2O_7 + 10H_2SO_4 = 4KHSO_4 + 2Cr_2(SO_4)_3 + 8H_2O + 3O_2.$$

Chromium trioxide decomposes when heated, although a little sublimes unchanged : $4CrO_3 = 2Cr_2O_3 + 3O_2$, and potassium dichromate (m.p. 396°) when strongly heated evolves oxygen : $4K_2Cr_2O_7 = 4K_2CrO_4 + 2Cr_2O_3 + 3O_2$.

Potassium permanganate explodes violently when warmed with concentrated sulphuric acid, but on dropping a solution of the permanganate in

dilute sulphuric acid into hydrogen peroxide solution, pure oxygen is evolved (Lindner, 1885): $2MnO_4' + 5H_2O_2 + 6H^{\cdot} = 2Mn^{\cdot\cdot} + 8H_2O + 5O_2$.

EXPT. 1.—A solution of 5 g. of $KMnO_4$ in a cooled mixture of 100 c.c. of water and 50 c.c. of concentrated sulphuric acid is dropped into 100 c.c. of "20 volumes" hydrogen peroxide in a flask.

Oxygen is evolved when water is dropped on a mixture of barium peroxide and potassium ferricyanide (Kassner, 1889):

$$BaO_2 + 2K_3Fe(CN)_6 = K_6Ba[Fe(CN)_6]_2 + O_2,$$

and when ferric chloride solution is dropped on barium peroxide:

$$6BaO_2 + 4FeCl_3 + 6H_2O = 6BaCl_2 + 4Fe(OH)_3 + 3O_2.$$

A mixture of 25 g. of powdered potassium chlorate and 5 g. of powdered manganese dioxide (*oxygen mixture*) evolves oxygen rapidly when heated at about 250°, *i.e.* below the m.p. of the chlorate. The heating must be carefully controlled, as the decomposition of the chlorate evolves heat and the reaction may become very violent. No perchlorate is formed (Mitscherlich, 1841; Eccles, *J.C.S.*, 1876, **29**, 857). The manganese dioxide acts as a catalyst; it undergoes no permanent chemical change and may be recovered by washing the residue with water.

EXPT. 2.—The oxygen mixture is placed in a wide test-tube, which is tapped so as to leave a free passage for the gas. The tube is connected by ¼ in. delivery tube with a wash-bottle of sodium hydroxide solution to remove any chlorine from the gas. The tube is gently heated with a slightly luminous Bunsen flame, beginning at the end near the cork and moving towards the closed end as the reaction proceeds. If the evolution of gas becomes violent, the flame is withdrawn. The gas is collected over water in jars, or in a metal Pepys' gas-holder (Fig. 266). When the gas is collected the lower opening is closed with a screw cap. Jars may be filled in the upper trough by opening the taps *A* and *B*.

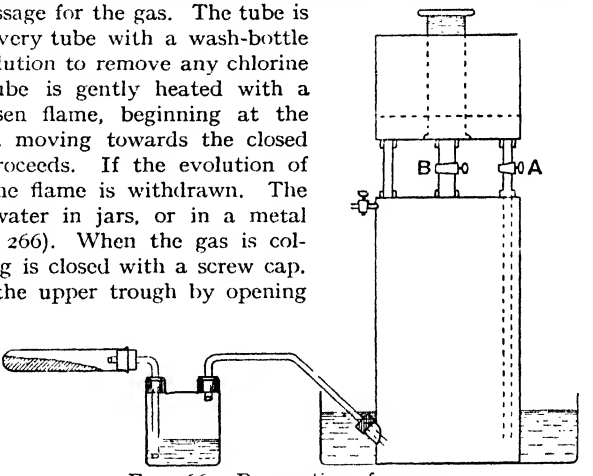


FIG. 266.—Preparation of oxygen.

Warning.—Manganese dioxide adulterated with powdered coal or antimony sulphide explodes violently on heating with chlorate. Many serious accidents (some fatal) have been caused in this way and a *little* of the mixture should always be heated in an open test-tube before beginning the experiment to make sure that no deflagration occurs.

Catalysis.—Some metallic oxides, such as copper oxide, ferric oxide, and manganese dioxide, act as catalysts in the decomposition of potassium chlorate. The action of manganese dioxide was discovered by Döbereiner in 1820, and

he supposed it to be a " contact " or surface action. Baudrimont in 1871 (*J.C.S.*, 1871, **24**, 1151) examined a number of substances and showed that the catalytic action is specific, which suggests that the catalyst takes part in *a cycle of chemical changes* (p. 144) by formation of intermediate compounds and not merely by contact (cf. Burrows and Brown, *J.A.C.S.*, 1923, **45**, 1343; 1926, **48**, 1790; McLaughlin and Brown, *ibid.*, 1928, **50**, 782). The manganese dioxide or other catalyst may take oxygen from the chlorate to form a higher state of oxidation, which then decomposes into oxygen and the original catalyst: $KClO_3 + 2MnO_2 = KCl + Mn_2O_7 = KCl + 2MnO_2 + 1\frac{1}{2}O_2$.

Fowler and Grant (*J.C.S.*, 1890, **57**, 272) showed that only oxides which can form unstable higher acidic oxides act catalytically: MnO_2 (forming Mn_2O_7), $Cr_2O_3(CrO_3)$, $Fe_2O_3(FeO_3)$, $CuO(CuO_2)$. These higher oxides are either known or exist in salts. Oxides (*e.g.* ZnO,MgO) which do not form such oxides act only feebly (to the same extent as powdered glass) and behave as porous bodies; acidic oxides not forming higher oxides (Al_2O_3, V_2O_5, WO_3) evolve both oxygen and chlorine: $K_2O,Cl_2O_5 + WO_3 = K_2O,WO_3 + Cl_2O_5 = K_2WO_4 + Cl_2 + 2\frac{1}{2}O_2$.

EXPT. 3.—Fuse about 10 g. of potassium chlorate in each of two hard glass test-tubes. To one add a *small* quantity of finely powdered manganese dioxide (or better, Mn_3O_4) and to the other a small quantity of Cr_2O_3. It is seen that: (i) oxygen is rapidly evolved, (ii) the fused salt becomes permanently pink ($KMnO_4$) and yellow (K_2CrO_4), respectively. $KMnO_4$ cannot exist alone at the temperature of the fused chlorate, as it decomposes at 240°. A little ferric oxide produces a violent effervescence and on cooling the mass is slightly pink, from the formation of ferrate K_2FeO_4.

McLeod (*J.C.S.*, 1889, **55**, 184; 1894, **65**, 202) observed that pieces of manganese dioxide in fused chlorate break up into very fine powder. The *physical* state changes, which suggests that the oxide enters into reaction and is reproduced. The manganese dioxide is not quite completely recovered by washing the residue after heating and is more finely divided and brown. McLeod suggested that chlorine and potassium permanganate are intermediate products:

$$2KClO_3 + 2MnO_2 = 2KMnO_4 + Cl_2 + O_2$$
$$2KMnO_4 = K_2MnO_4 + MnO_2 + O_2$$
$$K_2MnO_4 + Cl_2 = 2KCl + MnO_2 + O_2.$$

Although traces of chlorine (0·0375 p.c. of that in the chlorate) are evolved, the residue does not contain any manganate, as would be expected. McLeod found that if potassium carbonate (absorbing chlorine) is added to oxygen mixture the evolution of oxygen is retarded.

Manganese dioxide may act on *solid* chlorate, since the catalytic effect occurs below the fusion point. Some local fusion probably occurs on account of the heat evolved in the reaction (flashes of light are seen). L. H. Parker (*J.C.S.*, 1914, **108**, 1504; 1918, **113**, 396) has shown that chemical reaction may occur between solids. The reactions: $BaCO_3 + Na_2SO_4 \rightleftharpoons BaSO_4 + Na_2CO_3$ take place to some extent when the dry powder is heated short of fusion, or triturated in a dry mortar. Reaction also occurs when the dry powder is strongly compressed, as was shown by Spring (1885–6).

Technical production of oxygen.—Many processes have at various times been used for the preparation of oxygen on the large scale, but only two are now important: (i) the main process of *the fractional distillation of liquid air*, and (ii) to a small extent by *the electrolysis of water*.

A *chemical process* formerly used was the *Brin process* (p. 126). Some old *physical processes* were (i) the preferential solubility of oxygen from air by water under pressure (Mallet, 1869; see p. 56); (ii) the preferential dialysis of oxygen through an unvulcanised rubber membrane: Graham (1866) found that oxygen passes through 2½ times as fast as nitrogen, and by pumping air through a rubber bag by a mercury pump he obtained a gas containing 42 p.c. of oxygen; (iii) atmolysis, by passing air slowly through a porous clay tobacco-pipe stem enclosed in a partly exhausted outer tube, when the nitrogen diffuses out faster than the oxygen (Graham, 1863); (iv) since oxygen is slightly heavier than nitrogen, Mazza (1901) tried unsuccessfully to separate the gases in a centrifugal sieve.

Mere evaporation of liquid air would lead to serious loss of oxygen, as is seen from the following table, giving the results of Linde's experiments:

P.c. liquid not evaporated	P.c. oxygen in liquid by weight	P.c. oxygen in gas evaporating	P.c. original oxygen left in liquid
100	23·1	7·5	100
50	37·5	15	80
30	50·0	23	65
20	60·0	34	52
15	67·5	42	43
10	77·0	52	33
5	88·0	70	19

The gas from fresh liquid air contains only 7·5 p.c. of oxygen and when the liquid contains 50 p.c. of oxygen, or about two-thirds has evaporated, the gas is ordinary air. When 95 p.c. of the liquid has disappeared the gas contains 70 p.c. of oxygen, and if the remaining liquid is evaporated to produce 88 p.c. oxygen, we recover only 19 p.c. of the oxygen originally present.

The composition of liquid and gas phases of oxygen-nitrogen mixtures at 1 atm. pressure is also shown in Fig. 267 (Baly, *Phil. Mag.*, 1900, **49**, 517; Dodge and Dunbar, *J.A.C.S.*, 1927, **49**, 591).

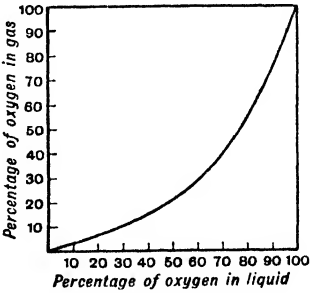


FIG. 267.—Compositions of gaseous and liquid oxygen-nitrogen mixtures in equilibrium.

The separation of liquid air into gaseous oxygen and nitrogen is carried out by a process of *fractional distillation*, with the use of a rectifying column as explained on p. 60. The escaping gas is scrubbed by nearly pure liquid oxygen passing down the column in the opposite direction (Linde, 1902).

Claude in 1906 introduced two new principles: (1) he liquefied the air in stages, obtaining two liquids, one rich in oxygen and the other in nitrogen,

(2) the expanding gas was allowed to work an engine, and the heat equivalent of this work was taken from it. (This had been previously suggested by Rayleigh.) A tall rectifying column is used, liquid rich in nitrogen being discharged into the top, whilst liquid rich in oxygen is introduced lower down, where the descending liquid has nearly the same composition.

In Claude's apparatus (Fig. 268) air at about 20–35 atm., cooled by an interchanger (p. 40), enters *A* already partly liquefied and passes through two sets of vertical pipes. The first drain into *A* and the second form a ring round the first and drain into *C*. Both sets are immersed in the bath *S* which, when the machine is operating, contains nearly pure liquid oxygen. The compressed air rises in the central group of tubes in *S*, and a liquid rich in oxygen condenses, which drains into *A*. The gaseous residue passes through the outer ring of tubes, is liquefied in them, and the liquid rich in nitrogen falls into an annular tube and pot *C*. This liquid is taken to the top of the column, that in *A* to a lower compartment *L* containing scrubbed liquid of the same composition. Gas rich in nitrogen passes from the top of the column and its cold is used in interchangers. The liquid condensed in the inner tubes in *S* is scrubbed by the air passing on.

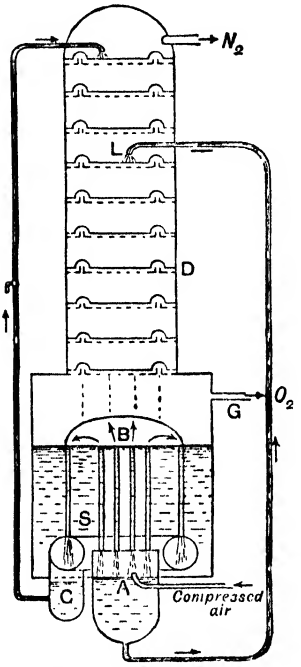


FIG. 268.—Claude's oxygen apparatus.

The heat of condensation of the compressed air evaporates the liquid oxygen in *S*, part of the vapour going up the rectifying column *D* in which it is mostly condensed, the heat of condensation displacing nitrogen from the liquid, which flows into *S*. The oxygen gas from *S* goes off by *G* to the heat interchanger, where its cold is utilised, after which it is pumped under pressure into steel cylinders for sale.

Liquid air usually contains 50–60 p.c. of oxygen (as compared with 23 p.c. in gaseous air). Liquid air and liquid oxygen are stored in spherical metal vacuum vessels holding 5–30 galls., the inner vessel being suspended by a thin metallic neck and the annular space exhausted. A high vacuum is produced by means of a tube of absorbent charcoal, open at the end exposed to the vacuous space and with the other (closed) end immersed in the liquid air itself. The daily rate of loss does not exceed 5 p.c.

About 85 p.c. of the commercial oxygen gas is used, in about equal amounts, in blowpipes for welding and for cutting metals (p. 286). The rest is partly used in medicine for cases of pneumonia, gas-poisoning, etc., and mixed with nitrous oxide, ether vapour or other anaesthetics. Some carbon dioxide is often mixed with it, since this stimulates breathing, and carbon dioxide alone is also used in cases of poisoning and collapse for the purpose of restoring respira-

tion. Oxygen is also used for oxidising linseed oil, maturing spirit, converting acetaldehyde into acetic acid, making synthetic nitric acid, and soaked as liquid in powdered charcoal as an explosive. Oxygen must also be supplied to aviators at high altitudes.

Properties of oxygen.—*Oxygen gas* is colourless, odourless, and tasteless, and supports respiration. Its normal density is 1·4290 g./lit., critical temperature −118·75°, critical pressure 49·7 atm. It is only sparingly soluble in water (p. 57).

Liquid oxygen, b.p. −183·0°, is pale blue and is quite strongly magnetic (the gas is also paramagnetic). It is supposed that about 50 p.c. of the liquid consists of O_4 molecules (G. N. Lewis, *J.A.C.S.*, 1924, **46**, 2027; Guillien, *Compt. rend.*, 1934, **148**, 1223, 1486). *Solid oxygen*, m.p. −218·4°, is also blue, and two other different crystalline forms exist at temperatures (−223° and −252°) below the melting point (Giauque and Johnston, *J.A.C.S.*, 1929, **51**, 2300). The solid is obtained by cooling the liquid in liquid hydrogen; it cannot be obtained by the rapid evaporation of the liquid.

The combination of substances with oxygen, when attended with the evolution of heat and light, is called *combustion*. Substances which burn in air do so with great brilliancy in pure oxygen, since the nitrogen in air acts as a diluent, absorbing part of the heat given off in the combustion.

A *glowing chip* is rekindled in oxygen gas and a *candle* burns in it very brightly. *Sulphur* burns with a bright blue flame forming mostly gaseous sulphur dioxide, with a little solid trioxide. *Phosphorus* burns with a blinding white light forming white solid phosphorus pentoxide. *Charcoal* burns brightly (sometimes, especially bark charcoal, giving off sparks) forming gaseous carbon dioxide. These are *acidic oxides*, forming acids with water. (Carbonic acid is a very weak acid.)

Heated *sodium* and *potassium* burn in oxygen with yellow and lilac flames, respectively, forming yellow and orange-red solid *peroxides*, Na_2O_2 and KO_2, which evolve oxygen with water and form alkali hydroxides. *Magnesium* and *calcium* burn with intense white light, forming the oxides MgO and CaO, which with water form $Mg(OH)_2$ and $Ca(OH)_2$, and are *basic oxides*.

A spiral of *iron* wire tipped with a bit of burning wood burns in oxygen; steel wire throws off sparks; black Fe_3O_4 is formed in fused globules which crack the bottom of the bottle unless it contains a layer of sand (Ingen-Housz's experiment).

A jet of *hydrogen* burns with a pale flame in oxygen, forming water, which condenses on the sides of the jar. A jet of oxygen passed into a jar of hydrogen burning at the mouth inflames and burns in the hydrogen (Fig. 269). The terms "combustible gas" and "supporter of combustion" are, therefore, relative.

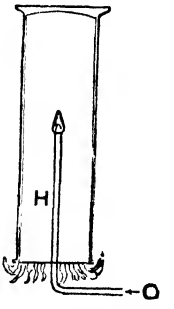


FIG. 269.—Combustion of oxygen in hydrogen.

EXPT. 4.—Dry barium or strontium chlorate is heated in a vertical spoon until it evolves oxygen freely, and a globe full of coal gas is lowered over

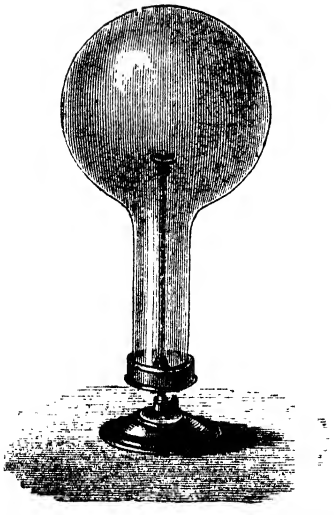


FIG. 270.—Apparatus for combustion.

the spoon (Fig. 270). The oxygen from the chlorate burns in the coal gas with a flame coloured green or crimson by the barium or strontium, respectively.

Oxides belong to different groups, classified as follows:

(i) *Acidic oxides* (SO_2, SO_3, P_2O_5, CO_2, SiO_2, etc.) react with bases to form salts containing the element of the acidic oxide in the anion.

(ii) *Basic oxides* (Na_2O, CaO, FeO, PbO, etc.) react with acids to form salts in which the element of the oxide is in the cation. In general, if a metal forms more than one oxide, the lower oxide is more basic (FeO, Fe_2O_3), but not always (CuO is more basic than Cu_2O).

(iii) *Amphoteric oxides* (ZnO, Al_2O_3, etc.) act as weakly basic oxides in presence of strong acids, and weakly acidic oxides in presence of strong bases.

(iv) *Higher oxides* include *dioxides*, which are often classified into (*a*) *peroxides* or *superoxides* when they contain the —O—O— group and (usually) give hydrogen peroxide with acids (Na_2O_2, BaO_2, etc.), and (*b*) *dioxides* or *polyoxides* when the oxygen atoms are linked separately by double bonds (O=Mn=O, O=Pb=O, etc.).

(v) *Neutral oxides* (CO, NO, N_2O, H_2O, etc.) do not function as acidic or basic oxides and are not peroxides.

(vi) *Suboxides* (C_3O_2, etc.) is a name rather loosely given to oxides containing less oxygen than the common lowest stable oxide.

(vii) *Mixed oxides* may be regarded as compounds of two oxides in which the element shows different valencies ($Pb_3O_4 = 2PbO, PbO_2$, $Fe_3O_4 = FeO, Fe_2O_3$, etc.).

Some substances, such as liquid zinc ethyl, finely divided phosphorus and some finely divided (*pyrophoric*) metals ignite spontaneously in air or oxygen.

EXPT. 5.—Precipitate a solution of lead acetate with a solution of tartaric acid, filter, wash and dry the precipitate of lead tartrate. Small portions are placed in narrow tubes sealed at one end and drawn out at the other. The tartrate is heated until fumes are no longer evolved, and the tubes are sealed. If a tube after cooling is cut with a file and the finely divided *pyrophoric lead* shaken out, the metal glows brightly forming yellow fumes of lead oxide PbO.

Some substances such as phosphorus oxidise slowly in air without taking fire, because the heat produced is dissipated. Oily cotton-waste, however, may ignite if stored in heaps exposed to air.

Oxygen is *absorbed* from gaseous mixtures by: (i) an alkaline solution of pyrogallol, which turns black (160 g. KOH, 10 g. pyrogallol, 130 c.c. of water); (ii) moist phosphorus (does not glow in pure oxygen); (iii) acid chromous chloride solution: $4CrCl_2 + O_2 + 4HCl = 4CrCl_3 + 2H_2O$ (some hydrogen may be

evolved) ; (iv) by mixing with excess of hydrogen and passing the non-explosive mixture over platinised asbestos at a dull red heat, or gently heated palladium, when water is formed and one-third of the contraction of the gas represents the oxygen contained in it : $2H_2+O_2=2H_2O$ (liquid).

Atomic oxygen.—The oxygen molecule is very stable and dissociates appreciably only at very high temperatures : $O_2=2O-116{\cdot}4$ k. cal. (absorbed). The calculated percentage dissociations at 760 mm. pressure are :

$T°$ abs.	2000	2500	3000	3500	4000
	$3{\cdot}6\times10^{-2}$	0·85	5·95	24·9	61·0

Atomic oxygen is formed (about 20 p.c.) by an electric discharge in oxygen at low pressure. It has very little action on H_2 and CO ; HCl is partly decomposed but HBr is completely oxidised to bromine and water. Ammonia forms an explosive substance, chlorine is oxidised to Cl_2O and ClO_2 and bromine to BrO_2 (Wrede, 1929 ; Harteck and Kopsch, 1930 ; Schlenk and Jablonowski, 1939).

Ozone

Van Marum in 1785 noticed that air near an electrical machine in active operation acquires a peculiar " electric " smell and tarnishes mercury. Cruickshank in 1801 noticed the same smell in electrolytic oxygen. In 1840 Schönbein proved that the smell is due to a peculiar gas, which he called *ozone* (Greek *ozo*, I smell), also produced by the slow oxidation of phosphorus in moist air, which liberates iodine from potassium iodide and is destroyed on heating.

EXPT. 5.—Place a few sticks of freshly scraped phosphorus in a stoppered bottle with a little water. When the fumes subside, introduce a piece of paper dipped into a solution of potassium iodide and starch (" starch-iodide paper "). This is turned blue. The peculiar smell of the gas is also noticed. The ozonisation is most pronounced at 24° ; below 6° no action occurs, except under reduced pressure. A greenish phosphorescent light, which can be seen in the dark, accompanies the formation of ozone.

Ozone occurs in traces in air, London air containing 1 part per million by volume (Paneth, 1937). Some effects attributed to ozone are caused by hydrogen peroxide or oxides of nitrogen. There is spectroscopic evidence for the existence of ozone in the upper atmosphere, where it may be formed by the action of ultra-violet light on oxygen. The evaporation of salt water in the form of spray is said to produce ozone in sea air. If present in air in larger amounts than 1 in 20,000 by vol. ozone is irritant and poisonous.

Ozone is contained in electrolytic oxygen, and in oxygen evolved by the action of fluorine on water and by the action of concentrated sulphuric acid on barium peroxide. It is produced by heating crystalline periodic acid, by passing oxygen over heated manganese dioxide, by the action of α-rays on oxygen, and by heating ammonium persulphate with nitric acid.

Ozone is formed from molecular oxygen with absorption of energy :

$$3O_2=2O_3-2\times34 \text{ k. cal.}$$

It would be expected to be stable at very high temperatures if formed in this way, and it is formed when a platinum wire or Nernst filament is strongly heated electrically under liquid oxygen, or when a hydrogen or carbon monoxide flame plays on liquid oxygen. The formation may involve atomic oxygen (Riesenfeld, 1924; Harteck, 1932): $O + O_2 = O_3$. Traces are formed in flames of hydrogen, acetylene or coal gas, but not carbon monoxide. It was supposed to be formed by the slow combustion of ether vapour on glowing platinum wire, but the substance produced is probably hydrogen peroxide.

Ozone is formed when oxygen (or air) is exposed to ultra-violet light. If a quartz mercury lamp is operated under a glass bell-jar for a few minutes, the air in the jar smells strongly of ozone. This gas does not contain oxides of nitrogen. Liquid oxygen exposed to ultra-violet light becomes dark blue, owing to the production of liquid ozone.

Warburg (1921) found that ultra-violet light of wave-length 209 mμ produces ozone, and since the line 185 mμ is the only one from the mercury lamp strongly absorbed by oxygen it is probably the chemically active one, corresponding with the energy 165 k. cal. This could dissociate the O_2 molecule into normal atoms (116 k. cal.). Warburg found that *two* molecules of ozone are formed per absorbed quantum. The formation of ozone, both by the electric discharge and by ultra-violet light, probably involves the dissociation of an oxygen molecule into atoms, which then react with two other oxygen molecules to form ozone: $O_2 = O + O$; $O_2 + O = O_3$. This agrees with the quantum yield found by Warburg if one molecule is dissociated per quantum: $O_2 + h\nu = 2O$.

Ozonised oxygen (or ozonised air) is prepared most conveniently by the action of a *silent electric discharge* on oxygen (or air), preferably dry. The preparation of pure ozone is described on p. 664.) Many types of **ozoniser** are used, all very similar in principle. One of the best and simplest (Fig. 271) is that of Brodie (1872), which is sometimes called Berthelot's ozoniser.

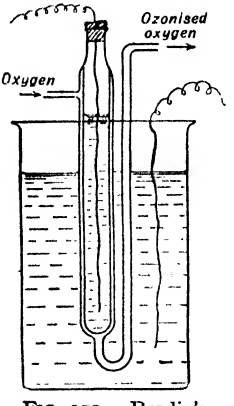


FIG. 271.—Brodie's ozonizer.

EXPT. 6.—A slow current of oxygen dried by bubbling through concentrated sulphuric acid is passed through the annular space between two thin glass tubes, the inner tube being filled with water or copper sulphate solution and the outer tube immersed in a jar of the same liquid, which keeps the apparatus cool. Wires from a coil dip into the liquids, which serve as electrodes. A bluish-violet glow is seen on the glass surfaces and usually a hissing noise is heard, but there should be no sparks, as these destroy ozone. The gas is conducted away through glass tubes connected with ground joints or joints made with bored ordinary corks, or paraffin wax. Rubber stoppers or tubing must not be used, as these are quickly destroyed by ozone. Air may be used instead of oxygen, but the yield is less good and the gas may contain oxides of nitrogen.

The Siemens ozoniser (1858) has two concentric glass tubes, the outer covered and the inner lined with tinfoil, but Brodie's apparatus is better. A simple ozoniser (von Babo's) is a straight glass tube with a platinum wire running inside and a spiral of copper wire outside to serve as electrodes.

With a good ozoniser cooled at 0° and a powerful coil, but no sparks, as much as 25 p.c. by weight of oxygen may be converted into ozone, but 12 p.c. is the average yield.

The **Siemens and Halske ozoniser** (Fig. 272), used on the large scale, consists of a battery of glass or porcelain tubes with internal aluminium tubes, enclosed in an earthed iron tank of water to cool the apparatus. The aluminium tubes are charged to a potential of 8000–10,000 volts, each battery of 6–8 tubes requiring half a kilowatt. High frequency increases the yield (Starke, 1923). The **Ozonair apparatus** consists of two sheets of aluminium gauze separated by a plate of insulator, several units being enclosed in a case and alternate plates charged and earthed. The best production amounts to about 40–60 g. of ozone per kilowatt-hour, at a concentration of 2 g. of ozone per cu. m. of air. With pure oxygen the yield is 120–180 g. The yields are about 5 and 15 p.c. of the theoretical with air and oxygen, respectively.

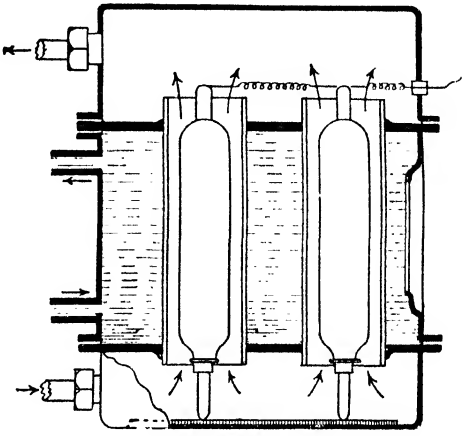


FIG. 272.—Siemens and Halske ozoniser.

Ozonised oxygen is formed at the anode by the electrolysis of diluted sulphuric acid (s. g. 1·1.) A good yield is obtained with a heavy current and an anode of a narrow platinum tube coated with glass, having a narrow line of metal exposed, and cooled by a stream of calcium chloride solution at −14° (Fischer and Massenez, 1907).

Formula of ozone.—Schönbein found that ozonised oxygen passed through a glass tube at 400° loses its smell and oxidising properties, and forms ordinary oxygen.

EXPT. 7.—Attach a hard glass tube by a cork joint to the ozoniser and heat the tube with a Bunsen flame. The issuing gas no longer acts on KI-starch paper. On cooling the reaction appears again.

Marignac and de la Rive (1845) and Shenstone and Cundall (1887) found that pure dry oxygen can be ozonised by an electric discharge. Briner and Durand (1907) converted a confined volume of pure oxygen completely into a blue liquid mixture of ozone and oxygen by the silent discharge in a tube cooled in liquid air. Thus, *ozone is a modification of oxygen.*

Andrews (1856) dried ozonised oxygen by sulphuric acid and passed it through two bulb-tubes, *A* containing potassium iodide solution, and *B* concentrated sulphuric acid (to retain water vapour). The increase in weight of the two bulbs was exactly equal to the oxygen equivalent ($O=I_2$) of the iodine

liberated. The bulb *A* was then replaced by a glass tube heated at 400°. The weight of the bulb *B* remained constant, showing that the gas contained no hydrogen. Andrews also found that ozone prepared in different ways (electric discharge, electrolysis, oxidation of phosphorus) has the same properties.

Andrews and Tait (1860) filled a tube *A* (Fig. 273) with dry oxygen, which communicated with a sulphuric acid manometer *B*. (Sulphuric acid has no action on ozone, *which attacks mercury*.) After the silent discharge, a maximum contraction of one-twelfth was observed. After the tube was heated to 300° the original volume was restored. Mercury in a glass bulb broken inside the tube by a short length of glass rod shaken on it was converted into a black powder and a variable volume of gas remained. A bulb of potassium iodide solution broken in the gas produced iodine, and the volume of gas remained unchanged although it no longer expanded after heating to 300°, and was therefore completely converted into oxygen. These experiments show that *ozone is denser than oxygen*, and is O_{2+n}.

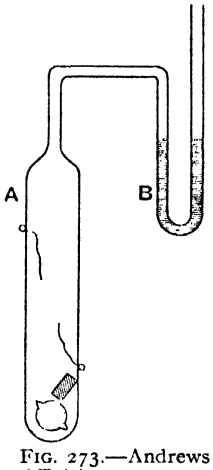


FIG. 273.—Andrews and Tait's experiment.

Odling in 1861 pointed out that the reactions could be explained if the formula is O_3 ($n = 1$):

$$2KI + O_3 \text{ (1 vol.)} + H_2O = 2KOH + O_2 \text{ (1 vol.)} + I_2.$$

The formula O_{2+n} will give the same result but O_3 is the simplest, and there were no experiments requiring a more complicated formula.

Odling's formula was confirmed by Soret in 1866–68 in two sets of experiments.* He pointed out that bodies which destroy ozone without change of volume, such as potassium iodide, give no indication of the density of ozone. In order to find the volume of ozone in a mixture with oxygen, some solvent or absorbent is necessary which takes up ozone without liberating oxygen (as is the case with potassium iodide).

Soret found that such absorbents were oil of cinnamon and oil of turpentine. He took two 250 c.c. flasks filled with ozonised oxygen over water (Fig. 274). In one flask the ozone was absorbed by turpentine, when dense white fumes were produced; in the other it was decomposed by heating the flask by a flame. The average contraction in the first flask was 6·26 c.c., almost double the average expansion of 3·26 c.c. (after cooling) in the second.

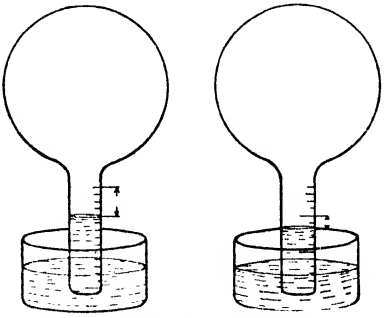


FIG. 274.—Soret's first experiment on ozone.

* "*Eau oxygénée et ozone*," in *Classiques de la Science* (III), A. Colin, Paris, 1913.

Ozone is decomposed by heat according to the equation : $2O_{2+n} = (2+n)O_2$. The contraction on absorption is 2 vols. ($2O_{3+n}$) and the expansion after heating is $(2+n)-2=n$ vols. Soret's experiment shows that these are in the ratio 2 : 1, hence $n=1$ and the formula of ozone is O_3.

EXPT. 8.—Newth's apparatus (Fig. 275) (1896) consists of two concentric glass tubes fitted together by a ground joint. The inner tube contains dilute sulphuric acid and the apparatus, previously filled with dry oxygen, is supported in a jar of water and crushed ice. Two wires from the coil dip into the liquids. By means of projections from the inner and outer tubes a thin sealed tube *a* containing oil of turpentine or oil of cinnamon is held in position in the annular space. The manometer containing concentrated sulphuric acid coloured with indigo communicates with the apparatus. The oxygen is ozonised. The contraction is read off on the gauge. The inner tube is twisted to break the tube of turpentine and after absorption the further contraction is read off. It will be found to be twice the contraction on ozonisation, *i.e.* double the expansion which would have occurred on decomposing the ozone by heat. *In each case, before reading the volume, adequate time must be allowed for the gas to assume a constant temperature.*

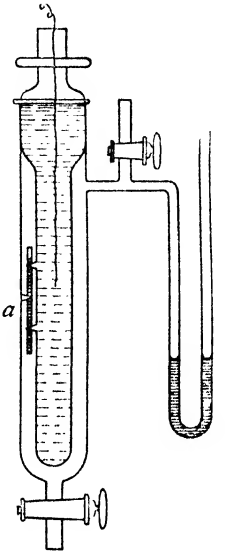


FIG. 275.—Newth's ozone apparatus.

Soret in his second research (1868) made use of *Graham's law of diffusion* (1833). If ozone is O_3 it should diffuse rather more slowly than carbon dioxide but more rapidly than chlorine. *The diffusion rates are in the inverse ratio of the square roots of the densities or molecular weights* :

$$\frac{\text{Rate of diffusion of } CO_2}{\text{Rate of diffusion of } O_3} = \frac{\sqrt{48}}{\sqrt{44}}; \quad \frac{\text{Rate of diffusion of } Cl_2}{\text{Rate of diffusion of } O_3} = \frac{\sqrt{48}}{\sqrt{71}}.$$

Soret allowed the gases to diffuse into pure oxygen and measured the **relative diffusion** v/V, where v is the volume of gas diffusing and V the total volume present in the original mixture of gas and oxygen. The rates of diffusion are proportional to the numbers of molecules in a given volume (measured by V) and inversely proportional to the square roots of the densities. The ratios v/V were therefore in the inverse ratio of the square roots of the densities or molecular weights of the diffusing gases.

The apparatus (Fig. 276) consisted of three glass tubes, B' B and C, placed over sulphuric acid in E and separated by sliding glass plates with holes, so that the tubes could be put in communication or separated. B' was filled with pure oxygen. B was first full of acid, and the mixture of one of the gases with oxygen, prepared in C (or else the ozonised oxygen), was transferred to B by sliding the glass partition o. The glass plates between B and B' had perforations, which could be brought between the two cylinders by sliding the plate o'. Diffusion

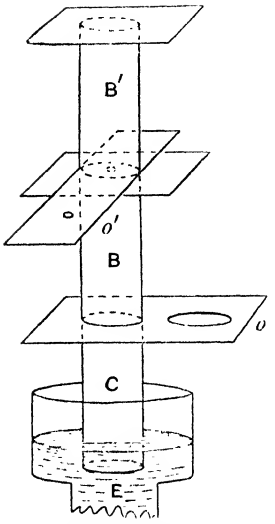


FIG. 276.—Soret's diffusion apparatus.

from B to B' was for forty-five minutes, when o' was slid back and the cylinders isolated. The gas in B' could then be driven out into a solution of baryta when carbon dioxide was diffused, or potassium iodide for chlorine or ozone. The ratio of the ozone in the original gas and in the gas in B' was determined from the amounts of iodine liberated by the gases. If u', u are the amounts of iodine liberated by the gas in B' and that remaining in B, respectively, then $v/V = u'/(u+u')$. The relative rates of diffusion were: chlorine 0·227, ozone 0·271, carbon dioxide 0·290.

The ratio of the values for chlorine and ozone is $227/271 = 0{\cdot}838$. The inverse ratio of the square roots of the molecular weights, assuming that ozone is O_3, is $\sqrt{48/71} = 0{\cdot}822$. The diffusion ratio for ozone and carbon dioxide is $271/290 = 0{\cdot}93$, whilst the inverse ratio of the square roots of the molecular weights is $\sqrt{44/48} = 0{\cdot}95$. The agreement is to 3 p.c., which is satisfactory, as the ozonised oxygen contained only 5 p.c. of ozone by volume.

In 1898 Ladenburg obtained nearly pure ozone by the evaporation of the liquid and compared the times of effusion of equal volumes of this gas and of oxygen in a Bunsen's effusion apparatus (p. 30); he found the molecular weight 44 (the gas contained some oxygen).

Riesenfeld and Schwab (*Ber.*, 1922, **55**, 2088), who were the first to obtain *pure* ozone (p. 664), determined the vapour density by Dumas' method (p. 17) and found the molecular weight 48, corresponding with O_3.

The formula O_3 was established beyond doubt by Brodie (*Phil. Trans.*, 1872, **162**, 435). He measured the volume of ozonised oxygen in a pipette over concentrated sulphuric acid, passed it through the reagent in a small bulb, and collected the oxygen in a glass cylinder containing mercury, the surface of which could be brought up to a vertical glass point inside the cylinder and the volume of oxygen calculated from the pressure. He found (i) the *contraction* C vols. on absorption, (ii) the *titre* T vols. or the expansion of the gas after heating to decompose the ozone, and (iii) the *oxidising effect* X in atoms of oxygen.

Let $C/T = R$ and $X/T = r$. All ozone reactions can be represented by the equation:

$$(p+q)O_{2+n} = qO_2 + [p(2+n)+qn][O], \quad \ldots\ldots(1)$$

where p, q and n are positive whole numbers. Hence $C = (p+q) - q = p$. If the ozone is decomposed by heat the equation is:

$$(p+q)O_{2+n} = [(p+q)+n(p+q)/2]O_2. \quad \ldots\ldots(2)$$

$$\therefore\ T = n(p+q)/2 \text{ vols., and } R = C/T = 2p/(p+q)n. \quad \ldots\ldots(3)$$

In finding the ratio X/T the titre in vols. must be multiplied by 2 to give atoms for comparison with X; $\therefore\ T = n(p+q)$ atoms;

$$\therefore\ r = [p(2+n)+qn]/(p+q)n = R+1. \quad \ldots\ldots(4)$$

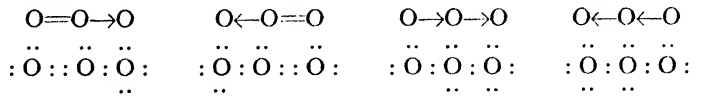
Brodie found four types of ozone reactions (apart from catalytic decomposition by alkalis), depending on the reagents used :

(1) Neutral KI, Ag foil, ($H_2O_2 + Na_2CO_3$), neutral $FeSO_4$, $R=0$ and $r=1$; (2) HI at 18°, ($Na_2S_2O_3$ + conc. Na_2CO_3), $R=1$, $r=2$; (3) conc. HI at 0°, conc. NaHS, K_2S, BaS, $R=\frac{3}{2}$, $r=\frac{5}{2}$; (4) turpentine, SO_2, neutral $Na_2S_2O_3$, ($Na_2S_2O_3$ + dil. Na_2CO_3), ($SnCl_2$ + HCl) at 0°, $R=2$, $r=3$. It is seen that (4) is always verified. The values of R are inserted into (3). The positive integral values of n which satisfy the resulting equation, with the condition that p and q are positive integers, are then calculated. The only formula which satisfies all the cases is O_3.

Case	R	Result from (3)	Possible values of n	Formula
1	0	$p=0$ $\therefore\ O_{2+n}=O_2+n[O]$	All positive integers	O_{2+n}
2	1	$2p=(p+q)n$ $p(2-n)=nq$	(i) $n=1$; $\therefore\ p=q$ $2O_3=O_2+4[O]$ (ii) $n=2$; $\therefore\ q=0$ $O_4=4[O]$	O_3 O_4
3	$\frac{3}{2}$	$p(4-3n)=3nq$	$n=1$; $\therefore\ p=3q$ $4O_3=O_2+10[O]$	O_3
4	2	$p(1-n)=nq$	$n=1$; $\therefore\ q=0$ $O_3=3[O]$	O_3

Riesenfeld and Egidius (*Z. anorg. Chem.*, 1914, **85**, 217) think there are only three types of ozone reaction, in which the oxidising effect per molecule is 0, 1 or 3. The first corresponds with the catalytic decomposition by alkalis : $2O_3=3O_2$, the second with potassium iodide : $O_3=O_2+O$, and the third with neutral thiosulphate and turpentine : $O_3=3O$. Brodie's other cases are combinations of these, *e.g.* by adding the second and third we find $2O_3=O_2+4O$ (Brodie's case 2).

The *structure* of ozone was usually taken as cyclic  , but this does not agree with its energy of formation from O_2, and Pauling (*J.A.C.S.*, 1932, **54**, 3581 ; Shand and Spurr, *ibid.*, 1943, **65**, 179) suggests resonance among four open-chain *bent* (isosceles triangle) structures (O—$\widehat{O}$—O angle 127°) :



Properties of ozone.—Ozonised oxygen does not usually contain more than 15 p.c. by vol. of ozone. By passing it through a tube cooled in liquid oxygen a cornflower-blue liquid separates, formerly thought to be liquid ozone. It is

a solution of oxygen in liquid ozone. On reducing the pressure on the cooled liquid, evaporation occurs and finally the liquid separates into an upper deep blue layer, which is a solution of ozone in liquid oxygen, and a lower violet-black layer, which is a solution of oxygen in liquid ozone. By pumping off the oxygen and fractional distillation of the ozone-rich layer, pure **liquid ozone**, very dark blue, b.p. $-112{\cdot}4°$, is obtained, and on careful evaporation this gives deep blue pure gaseous ozone (Riesenfeld and Schwab, *Ber.*, 1922, **55**, 2088). The vapour density in a small Dumas apparatus corresponded with O_3.

Liquid ozone is fairly stable below its b.p. and may be distilled in the absence of dust or organic matter, a trace of which causes explosion. The pure gas is stable in the absence of organic matter and catalysts, otherwise it explodes. It also explodes on heating. On cooling liquid ozone in liquid hydrogen, **solid ozone** is formed in violet-black crystals, m.p. $-249{\cdot}7°$.

Ozone mixed with oxygen decomposes slowly even at low temperatures; the decomposition is almost instantaneous at 300° and takes place in the gas phase according to the equation: $2O_3 = 3O_2$, and with phosphorescence. Moisture accelerates the change only slightly, but reduced pressure or the presence of chlorine, oxides of nitrogen, and phosphorus pentoxide accelerates the change markedly.

Ozone is more soluble than oxygen in water, 1 vol. of water at 0° dissolving 0·49 vols. of ozone. It is more soluble in glacial acetic acid and carbon tetrachloride, forming blue solutions.

Ozone has a remarkable action on mercury. If some mercury is shaken in a clean dry flask of ozonised oxygen, the metal loses its meniscus and adheres to the glass as a mirror. This is due to oxidation to Hg_2O, which dissolves in the mercury. On shaking with water, the mercury recovers its original form (Hodgson, *J.C.S.*, 1924, **125**, 462).

Ozone is catalytically decomposed by alkali solutions, metallic silver, platinum and palladium, by oxides of manganese, cobalt, iron and silver, and by shaking with powdered glass. Warm silver is blackened (especially if it has been rubbed with rusty emery paper), the oxides Ag_2O, AgO and Ag_2O_3 being formed (Manchot, 1907–9; Jirsa and Jellinek, 1926): this reaction is a specific test for ozone.

Ozone is *a powerful oxidising agent.* In a few reactions it reduces oxidised bodies by withdrawing an atom of oxygen: hydrogen peroxide reacts slowly: $H_2O_2 + O_3 = H_2O + 2O_2$, and barium peroxide is reduced: $BaO_2 + O_3 = BaO + 2O_2$, but ozone has no action on chromic acid or permanganate. In a few reactions the ozone molecule as a whole reacts, *e.g.* with stannous chloride:

$$3SnCl_2 + 6HCl + O_3 = 3SnCl_4 + 3H_2O$$

and sulphur dioxide: $3SO_2 + O_3 = 3SO_3$, but mostly only one atom of oxygen reacts, the rest of the ozone molecule being liberated as molecular oxygen. Ozone bleaches indigo and many other dyes, converts moist sulphur, phosphorus and arsenic into sulphuric, phosphoric and arsenic acids, oxidises ammonia to ammonium nitrite and nitrate, and ferrocyanide in solution into

ferricyanide: $2Fe(CN)_6'''' + H_2O + O_3 = 2Fe(CN)_6''' + 2OH' + O_2$. Moist iodine is oxidised to iodic acid: $I_2 + 5O_3 + H_2O = 2HIO_3 + 5O_2$, dry iodine to yellow I_4O_9: $2I_2 + 9O_3 = I_4O_9 + 9O_2$.

Halogens are liberated from their hydracids and iodine from neutral iodide solution, which becomes alkaline: $2I' + O_3 + H_2O = I_2 + 2OH' + O_2$. In presence of alkali some iodine forms iodide and iodate, but is liberated again on acidification. Alkaline iodide solution is oxidised to iodate and periodate.

The action of ozone on *acidified* potassium iodide gives very variable results. Brodie found an oxidising effect varying from 1·14 to 2·37 and noticed that oxygen also liberates iodine (for which he corrected); he took the average value 2. Ladenburg and Quasig (*Ber.*, 1901, **34**, 1184) supposed the first reaction to involve the formation of hydrogen peroxide: $4O_3 + 10HI = 3O_2 + 5I_2 + H_2O_2 + 4H_2O$, which liberates some iodine: $H_2O_2 + 2HI = 2H_2O + I_2$, so that the total reaction is: $4O_3 + 12HI = 3O_2 + 6I_2 + 6H_2O$. Luther and Inglis (*Z. phys. Chem.*, 1903, **43**, 203) found that 3 atoms of iodine are rapidly liberated per molecule of ozone and another atom slowly. Riesenfeld and Bencker (*Z. anorg. Chem.*, 1916, **98**, 167) also found hydrogen peroxide, and in the final reaction 3 atoms of iodine per molecule of ozone; but the oxidising effect was 1 to 2·7 and they regarded this as due to a superposition of two types of reaction:

$$X = 1 \quad 2HI + O_3 = I_2 + H_2O + O_2$$
$$X = 3 \quad HI + O_3 = HIO_3,$$

the HI and HIO_3 then reacting to form iodine. The H_2O_2 would then be formed by a side reaction, as it is only found in traces.

Ozone adds to organic compounds containing unsaturated linkages (including benzene) to form *ozonides*, which are decomposed by water, *e.g.* ethylene ozonide gives two molecules of formaldehyde together with hydrogen peroxide (Harries, 1905): $C_2H_4(O_3) + H_2O = 2H_2C{:}O + H_2O_2$.

A solution of ozone reddens litmus paper before bleaching it, and has been supposed to contain *ozonic acid*, $(HO)_2O{\rightarrow}O$. By the action of ozone on solid caustic potash a yellow peroxide is obtained, regarded by Baeyer and Villiger (1902) as *potassium ozonate*, but on acidification it does not give ozone but oxygen (Traube, 1912–16).

Ozonised air is used in sterilising water. It is bubbled through the filtered water in a tall column, 2 g. of ozone being used per cu. m. of water. It is also used for purifying air, *e.g.* in underground railways, and for oxidation reactions, *e.g.* for oxidising *iso*-eugenol to vanillin. There is some doubt as to the efficiency of its bactericidal action in dry air.

Tests for ozone.—The difficulty of detecting ozone when there is not enough to smell it (1 vol. in 500,000) is that halogens, hydrogen peroxide vapour, and some oxides of nitrogen (N_2O_3,NO_2,N_2O_4), also liberate iodine from potassium iodide. Paper wetted with potassium iodide and starch solution is, therefore, not specific in the detection of ozone. If half a piece of neutral litmus paper is wetted with potassium iodide solution, the wetted part is turned blue by ozone: $O_3 + 2KI + H_2O = 2KOH + O_2 + I_2$, whilst oxides of nitrogen do not affect it but turn the other half red. Test papers soaked in alcoholic solutions

of the following reagents give specific reactions (Arnold and Mentzel, *J.C.S.*, 1902, **82**, ii, 352, 691):

Reagent	Ozone	Oxides of Nitrogen	Chlorine or Bromine
Tetramethyl base -	violet	straw-yellow	deep blue
Benzidine - - -	brown	blue	blue, then red

Hydrogen peroxide does not affect the reagents. Hydrogen peroxide and oxides of nitrogen can be removed by passing the gas through chromic acid solution.

Hydrogen peroxide and ozone are decomposed by passing the gas through manganese dioxide, but oxides of nitrogen pass on and will decolorise dilute permanganate. The latter absorbs oxides of nitrogen but allows ozone to pass. Hydrogen peroxide is detected by bubbling the gas through a solution of potassium ferricyanide and ferric chloride, which is turned blue (Keiser and McMaster, *J.C.S.*, 1908, **94**, ii, 222).

The iodine liberated by ozone from *neutral* potassium iodide may be titrated with thiosulphate ($I_2 = O_3$) after just neutralising the alkali formed (Ladenburg and Quasig, 1901). Another method of determination depends on the oxidation of sodium nitrite solution (Usher and Rao, *J.C.S.*, 1917, **111**, 799): $NaNO_2 + O_3 = NaNO_3 + O_2$. (For determinations of ozone, H_2O_2, etc., see Edgar and Paneth, *J.C.S.*, 1941, 511.)

CHAPTER XXIII

WATER AND HYDROGEN PEROXIDE

Water

THE formation of water on the explosion of a mixture of hydrogen and air or oxygen was noticed by Priestley and Warltire (1781). Cavendish (1781–1784) showed that 2·01 vols. of hydrogen and 1 vol. of oxygen combine to form water, but the clear statement that water is composed of these substances is due to Lavoisier (1785). Nicholson and Carlisle, and Cruickshank, in 1800, found that water is decomposed into its elements by an electric current, hydrogen appearing at the negative and oxygen at the positive pole. No other substances are produced from pure water (Davy, 1806).

The *gravimetric composition of water* is determined by: (1) passing hydrogen over heated copper oxide; (2) burning weighed quantities of hydrogen and oxygen and weighing the water.

The *volumetric composition of water* is determined by exploding accurately measured volumes of hydrogen (in excess) and oxygen and measuring the volume of the residual hydrogen. (For accounts of the classical researches, see Partington, *The Composition of Water*, Bell & Sons, "Classics of Scientific Method," 1928).

The gravimetric composition of water.—Berzelius and Dulong (1819) passed dried hydrogen over heated copper oxide in a weighed tube: $CuO + H_2 = Cu + H_2O$, collecting the water in a weighed calcium chloride tube. The loss in weight of the copper oxide tube gave the weight of oxygen, and the hydrogen was found by difference. Three experiments gave 11·046 to 11·191 p.c. of hydrogen in water. In 1842 Dumas (*Ann. Chim.*, 1843, **8**, 189), assisted by Stas, carried out the experiment more accurately.

Hydrogen generated from zinc and previously boiled dilute sulphuric acid was purified by passing through seven U-tubes containing: (1) lead nitrate solution to remove hydrogen sulphide, (2) silver sulphate solution to remove arsenic hydride, (3) three tubes of caustic potash to remove acid vapours, (4) two tubes of sulphuric acid cooled in ice, or else phosphorus pentoxide, to dry the gas. The reagents were distributed on pumice or broken glass to expose a large surface. These tubes were followed by a *témoin* ("witness") tube containing sulphuric acid or phosphorus pentoxide, the weight of which must remain unchanged when the drying is as effective as possible.

The dry copper oxide was contained in a large hard-glass bulb with a long neck, weighed vacuous. The air was displaced from the apparatus by hydrogen, and the bulb heated by a large spirit lamp for ten to twelve hours. The water produced was collected in a bulb, the neck of which contained calcium chloride, followed by four drying tubes containing solid potash, and sulphuric acid on pumice, cooled in ice, or phosphorus pentoxide. The residual hydrogen escaped by bubbling through sulphuric acid. In all experiments the weight of the last absorption tube was constant. The apparatus is shown in Fig. 277.

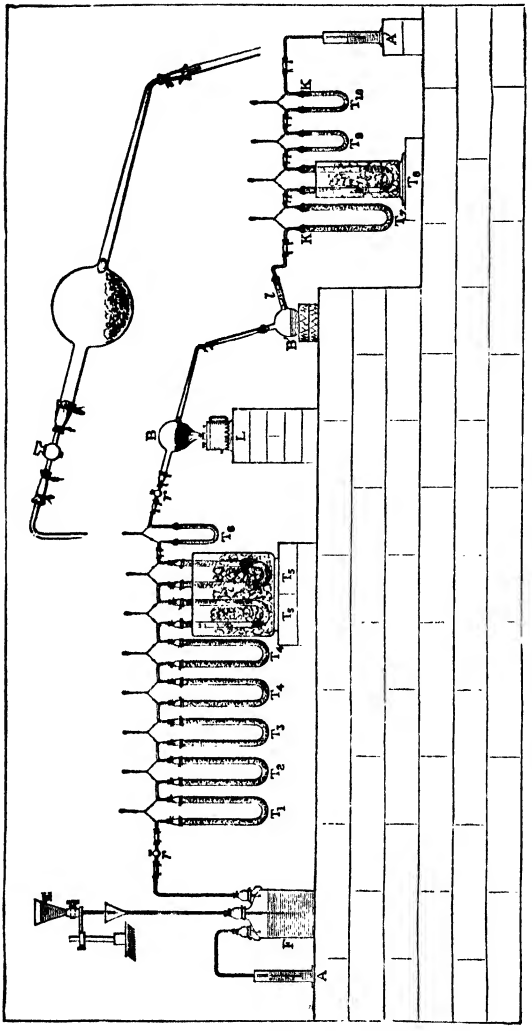


FIG. 277.—DUMAS' APPARATUS FOR DETERMINING THE COMPOSITION OF WATER.

The copper oxide bulb, B, is shown above on a larger scale. The apparatus consisted of the following parts: F, a Woulfe's bottle for the generation of hydrogen; E, a tap-funnel containing sulphuric acid; A, a mercury safety-valve; T_1, a tube containing lead nitrate solution spread on broken glass; T_2, a tube containing glass moistened with silver sulphate solution; T_3, a tube containing (*a*) pumice soaked in potash solution, (*b*) solid potash; T_4, T_4, tubes containing pieces of potash; T_5, T_5, tubes containing phosphorus pentoxide (or sometimes sulphuric acid spread over pumice, cooled in a freezing mixture); T_6, a *témoin* tube containing phosphorus pentoxide (or sulphuric acid and pumice); B, the bulb containing copper oxide, with stopcock and pointed tube delivering into the receiver B′, for collecting the water, with fragments of calcium chloride at *l*; L, a large spirit-lamp for heating the bulb; T_7, a tube of solid potash; T_8, a tube of phosphorus pentoxide (or sulphuric acid on pumice, cooled in a freezing mixture); T_9, a *témoin* tube of phosphorus pentoxide, or sulphuric acid; T_{10}, a guard-tube of phosphorus pentoxide (not weighed) to exclude moisture; A′, escape-valve for excess of hydrogen, containing sulphuric acid.

The copper was allowed to cool in a stream of hydrogen, the hydrogen displaced by air in the whole apparatus, and the bulb exhausted and weighed. The absorption system was also weighed.

A mean of nineteen experiments gave the following result:

	Weight p.c.	Weight ratio
Oxygen - - - - - - -	88·864	7·98
Hydrogen - - - - - - -	11·136	1·00
	100·000	8·98

Dumas recognised two errors in the method :

(1) Air dissolved in the dilute sulphuric acid was liberated with the hydrogen and its oxygen combined with hydrogen in the heated copper oxide bulb ;

(2) the reduced copper retained hydrogen when cooled in that gas.

Both errors decreased the loss in weight of the copper oxide bulb, and the proportion of oxygen should be too small. Dumas, influenced by Prout's hypothesis, believed the ratio of oxygen to hydrogen should be exactly 8·00 to 1, and the atomic weight of oxygen (H = 1) equal to 16·00. His observed value O = 15·96, however, was preferred. Dittmar and Henderson (1890–93), by recalculating Dumas' results, showed, however, that his value is lower than 15·96, and about 15·8.

Keiser (1888) weighed hydrogen occluded in palladium, pumped the gas over heated copper oxide, and weighed the water, the oxygen being found by difference.

W. A. Noyes (1890) burnt hydrogen in a copper oxide bulb and condenser made in one piece, the increase in weight of which gave the weight of hydrogen. The water was then removed and weighed, and the loss in weight of the apparatus gave the weight of oxygen. In a later research (*J.A.C.S.*, 1907, **29**, 1718), pure hydrogen was weighed in palladium in an exhausted tube (Fig. 278). Pure oxygen was admitted and the tube heated electrically. The steam formed condensed in a cooled leg of the tube. The tube and water were weighed and then connected with an apparatus to which the water was transferred and in which it was weighed, the residual gas being pumped off and measured and a correction made for it. Noyes also used copper oxide in the tube and admitted hydrogen, the results giving somewhat lower values for the atomic weight of hydrogen. The results with palladium and the purest hydrogen, from the electrolysis of baryta solution, gave H = 1·00787 if O = 16·0000.

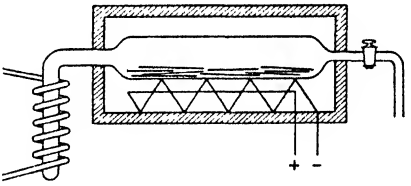


FIG. 278.—Noyes' apparatus.

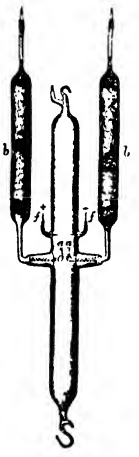


FIG. 279.—Morley's apparatus. The *dry* gases passed through phosphorus pentoxide tubes, *b*, *b*, to the jets, *a*, *a*, where they were ignited by electric sparks between wires from the electrodes, *f* and *f*.

E. W. Morley (*Smithsonian Contributions to Knowledge*, 1903, **29** ; *Z. phys. Chem.*, 1896, **20**, 417) weighed the hydrogen and oxygen, at first in large glass globes but later the hydrogen was weighed absorbed in palladium in a glass tube and driven out by heating. The very pure and dry gases were burnt at platinum jets *a a* in a previously exhausted glass combustion vessel (Fig. 279), the lower part being cooled in water ; the gases were kindled by electric sparks between platinum wires, *f f*. The water trickled down to

the lower part of the apparatus. The water was frozen and the residual gas (containing both hydrogen and oxygen) was pumped off through the P_2O_5 tubes *b b* (to keep back moisture) and analysed.

As a mean of twelve experiments, in which 400 g. of water in all were synthesised, Morley found the ratio O : H = 8 : 1·00762 ; if four low values are omitted the figure is 8 : 1·00768.

The volumetric composition of water.—The combining volumes of hydrogen and oxygen may be found by exploding a mixture of the gases with an excess of hydrogen over mercury in a Bunsen's eudiometer and measuring the volume of residual hydrogen ; by exploding a mixture of 2 vols. of hydrogen and 1 vol. of oxygen in a U-shaped eudiometer with the closed end surrounded by an amyl alcohol vapour jacket to keep the steam gaseous (Fig. 280) it is found that 2 vols. of steam are formed, all gases being measured over mercury at the same temperature and pressure. Hence : $2H_2 + O_2 = 2H_xO_y$. $\therefore$ $x = 2$ and $y = 1$ and the formula of steam is H_2O.

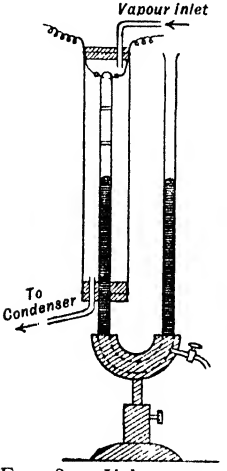


FIG. 280.—Volume composition of steam.

The early experiments are those of Cavendish (1781), who obtained the volume ratio H/O = 201 : 100, Gay-Lussac and Humboldt (1805) who found 199·89 : 100, and Bunsen, whose numerous determinations indicated an almost exact ratio of 2 : 1.

Alexander Scott, whose experiments, made in 1887–9 and 1893, at first yielded slightly varying ratios, from 199·4 : 100 to 200 : 100, showed in later experiments that this was due to a film of grease carried over from the stopcock lubrication into the eudiometer, which took up a little oxygen during the explosion, burning to carbon dioxide and steam. By using pure hydrogen prepared by passing steam over sodium, and pure oxygen from silver oxide, and by lubricating the stopcocks with syrupy phosphoric acid, the combining ratio at S.T.P. was found (*Phil. Trans.*, 1893, **184**, 543) to be 200·285 : 100. Moles (*Z. phys. Chem.*, 1925, **115**, 161 ; **117**, 157) recalculated this to 200·302 : 100.

Scott's apparatus (Fig. 281) consisted of a pipette *A* in which gas was measured over mercury and passed into a mixing container *H* over mercury. The mixed gas was exploded in portions by sparking over mercury in the eudiometer *J*, and the residual gas was measured in *A*.

Burt and Edgar (*Phil. Trans.*, 1916, **216**, 393 ; cf. Guye, *J. Chim. Phys.*, 1917, **15**, 208) in an elaborate research found as an average of 59 determinations 200·288 : 100, agreeing with Scott's to within 3 parts in 200,000. The special points of the research were : (1) very carefully purified gases were used, (2) the actual measurements were carried out at 0° and under 1 atm. pressure, so that the temperature and pressure corrections were eliminated.

The hydrogen, prepared by electrolysis of a solution of recrystallised barium hydroxide, was dried by phosphorus pentoxide and further purified: (i) by passing over charcoal cooled in liquid air, which adsorbed oxygen and nitrogen

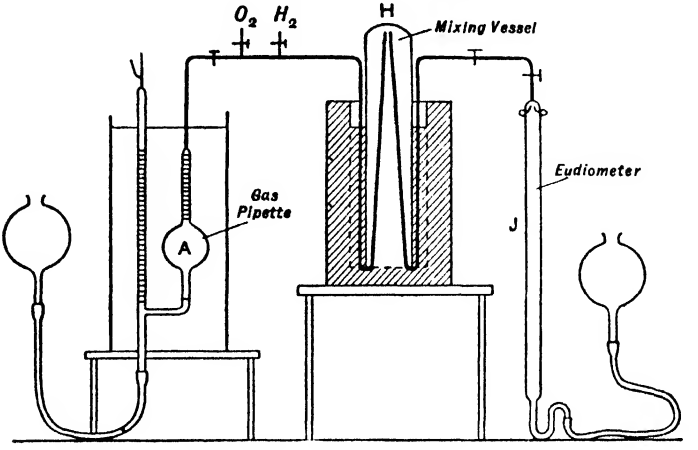


FIG. 281.—Scott's apparatus.

but hydrogen only slightly; (ii) by passing through a tube containing palladium black to convert oxygen to water, and then pumping the gas through the walls of a closed palladium tube heated electrically. The palladium tube was welded to a short platinum tube sealed into a glass tube. This was sealed inside a wider tube, and the palladium heated by a platinum spiral wound on a quartz cylinder slipped over it. The palladium was protected from mercury vapour from the pumps by plugs of gold wire sponge. The palladium was charged with hydrogen at 100°, 300 c.c. of gas were then pumped off at 180°, and the metal recharged with hydrogen at 100°.

The oxygen was prepared: (1) by the electrolysis of baryta solution, liquefaction in fresh liquid air, and fractionation; (2) by heating pure potassium permanganate in glass tubes and washing the gas (*a*) with strong caustic potash solution, (*b*) with saturated baryta solution, (*c*) with very strong potash solution. The gas was then dried by sticks of potash, and phosphorus pentoxide, liquefied, and fractionated.

The apparatus, part of which is shown diagrammatically in Fig. 282, consisted of a 300 c.c. glass pipette *A*, sealed to capillary tubes at each end. The lower capillary was expanded to a dead-space *B* about 1 c.c. capacity, with a glass levelling-point. The upper capillary led to a 3-way tap *C*. The pressure of the gas in the bulb was equal to the vertical distance between the mercury surface in *B* and that in the upper chamber *D*, also provided with a levelling-point, these two vessels being kept at a constant distance apart by a stout glass

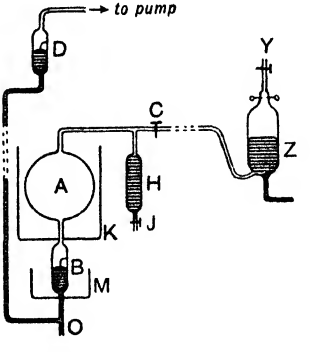


FIG. 282.—Burt and Edgar's apparatus.

rod sealed between them. The manometer head passed to a mercury pump. The tube *H* and tap *J* formed a *volume adjuster*; the capacity of the pipette *A* could be varied within narrow limits by withdrawing mercury from *J*, this mercury could be weighed, and its volume thus accurately determined. The bulb and upper part of the apparatus were enclosed in an ice-bath, the lower dead-space was surrounded by a small brine-bath *M*. The volume of the apparatus was determined by weighing the contained mercury.

The gas entered the pipette, displacing mercury through *O* into a levelling-bulb, until the surfaces in *B* and *D* stood at the glass-points. Since there was a vacuum above the mercury in *D*, the gas was measured under the pressure of a mercury column which was very approximately 1 atm. The fine adjustment was made by the volume adjuster *J*, by which small amounts of extra gas could be added to the pipette by running out mercury, which was weighed.

The gas was then passed to the explosion bulb *Z* of about 1 lit. capacity by opening *C* and raising the reservoir at *O*, mercury being displaced from *Z* through an air-trap. Two pipettes of hydrogen with a little excess measured by the volume adjuster *J* were thus passed into *Z*. A pipette *A* of oxygen was then added in portions, firing after each addition. The small residual volume of wet hydrogen was sparked for a few minutes. The vessel *Z* was then cooled by a mixture of solid carbon dioxide and acetone to freeze the water, the pressure reduced, and the residual gas taken off from *Y* by a mercury pump, passed through a drying train, and its volume measured as follows. The pipette *A* was filled with hydrogen and carefully levelled. The small volume of residual gas was then added and the pressure adjustment made by running a little mercury from *J*. From the weight of this mercury the volume of residual gas was calculated.

The weights of 1 litre of hydrogen and oxygen at S.T.P. are, according to Morley, 0·089873 g. and 1·42900 g. respectively. With these figures, the values of Burt and Edgar give, for the weight of oxygen combining with 1 part by weight of hydrogen,

$$\frac{1{\cdot}42900}{2{\cdot}00288 \times 0{\cdot}089873} = 7{\cdot}93868.$$

The atomic weight of hydrogen is therefore: 8·0000/7·9387 = 1·00773.

The average of Scott's result (as corrected by Moles) and Burt and Edgar's, is 2·00295, and with Morley's densities this gives H = 1·00776, which is about half-way between Morley's and Noyes's gravimetric values. The *mass spectrograph* value for normal hydrogen (containing some deuterium) is H = 1·0080 (cf. Swartout and Dole, *J.A.C.S.*, 1939, **61**, 2025).

Properties of water.—Water is purified by distillation, best in a copper still with a copper or pure tin condenser. Distilled water usually contains carbonic acid (pH about 6). Purer "conductivity" water is made in special stills (Bousfield, *J.C.S.*, 1905, **87**, 740; 1912, **101**, 1443; Bourdillon, *ibid.*, 1913, **103**, 791; Kraus and Dexter, *J.A.C.S.*, 1922, **44**, 2468; Bencowitz and Hotchkiss, *J. Phys. Chem.*, 1925, **29**, 705).

Still purer water is obtained by destroying the nitrogenous organic matter, which gives traces of ammonia on distillation, by passing chlorine through

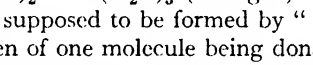
boiling distilled water for half an hour. The chlorine is boiled out, pure potash and potassium permanganate are added, and the water distilled, the first half being rejected and a quarter of the remainder collected.

A list of the main physical properties of water is given on p. 292. (See Dorsey, *Properties of Ordinary Water Substance*, New York, 1940.)

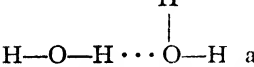
The vapour density of *steam* just above 100° is only slightly greater than corresponds with the formula H_2O and becomes normal when corrected for the deviation from Boyle's law (Levy, 1909; Nernst, 1910).

The properties of *liquid water*, however, are very abnormal: its high surface tension, high dielectric constant, great ionising power for solutes, high boiling point as compared with H_2S, the expansion on freezing, a maximum density at 4°, the decrease of compressibility and viscosity with increase of pressure, the minimum specific heat at about 30°, and the abnormal Trouton coefficient (p. 44), all differentiate water from so-called "normal" liquids (p. 45).

The abnormal properties of liquid water were ascribed to the presence of *associated molecules* $(H_2O)_2$ and $(H_2O)_3$ (Röntgen, 1891; Sutherland, 1900, etc.). These were later supposed to be formed by "hydrogen bonds," a pair of electrons on the oxygen of one molecule being donated to a hydrogen atom on another (Latimer and Rodebush, *J.A.C.S.*, 1920, **42**, 1419):



A *static* bond of this type, however, is forbidden by Pauli's principle, and hydrogen bonds must involve *resonance* (Pauling, *The Nature of the Chemical Bond*, 1940, 284; discussion, *Trans. Faraday Soc.*, 1940, **36**, 871), the *proton* oscillating between the attractive fields of two oxygen nuclei O—H—O, but nearer the one to which it is bound covalently, so that the hydrogen bond is largely ionic in character: it may be represented by a dotted line



and occurs in a number of "abnormal" hydrogen compounds. This case is sometimes called a *hydroxyl bond* to distinguish it from a hydrogen bond in, say, [F—H · · · F]′ (Bernal and Megaw, *Proc. Roy. Soc.*, 1935, **151**, 384). The hydrogen bond in many compounds has a characteristic infra-red absorption band.

Before discussing the structure of liquid water it is necessary to consider that of ordinary *ice* (for the various forms of ice, see p. 52). This is known from X-ray measurements (Barnes, *Proc. Roy. Soc.*, 1929, **125**, 670; Pauling, *J.A.C.S.*, 1935, **57**, 2680; *The Nature of the Chemical Bond*, 1940, 301). The structure is like that of β-tridymite with oxygen atoms in place of silicon, or like the wurtzite structure (Fig. 149), and hydrogen atoms (protons) unequally spaced among the oxygens. Each 4-coordinated oxygen ion has bonded at tetrahedral angles four oxygens at a distance 2·76 A. with a proton along each O—O axis, two chemically-bonded at a distance 0·99 A., and two hydrogen-bonded at a distance

1·77 A., from the oxygen (Cross, Burnham, and Leighton, *J.A.C.S.*, 1937, **59**, 1134). At −183° the Raman spectrum shows that there is almost complete coordination, four hydrogen bonds being formed by each molecule, but at 0° there are many molecules forming only three and two bonds. On fusion and further increase of temperature more bonds are broken, the average at 40° being two bonds per molecule. Pauling has shown that the specific heat data require a large number of configurations in an ice crystal, each corresponding to certain orientations of the water molecules, and the crystal can change from one configuration to another by rotation of some of the molecules or by the motion of some of the protons.

The X-ray spectrum also indicates that liquid water has a partly broken-down ice structure, with considerable coordination persisting through hydrogen bonds, which decreases with rise of temperature or addition of electrolytes (Bernal and Fowler, *J. Chem. Phys.*, 1933, **1**, 515; Katzoff, *ibid.*, 1934, **2**, 841; Morgan and Warren, *ibid.*, 1938, **6**, 666; Llewellyn, *J.S.C.I.*, 1940, **59**, 619; Pauling, *The Chemical Bond*, 1940, 304). The Raman spectrum is compatible with the presence of nine types of coordinated water molecules. In heavy water the degree of coordination is somewhat larger.

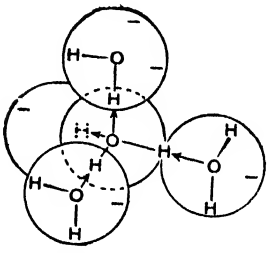


FIG. 283.—Structure of water.

Bernal and Fowler postulated a four-fold tetrahedral coordination about each water molecule (Fig. 283). The hydrogens (which practically lie inside the large oxygen spheres) are centres of positive charge, the other two apices of the tetrahedral arrangement being centres of negative charge, these charges holding the groups together. Since liquid water is denser than ice, it cannot be merely a disordered ice-structure (tridymite-like), and they supposed that it contains a disordered form of the denser quartz structure, the nature being "determined by different geometrical arrangements of the same molecules in small regions of the liquid due to different amounts of molecular movement imposed by the temperature."

NATURAL WATERS

The composition of *natural waters* (rain, river, spring, sea and mineral waters), and the methods of softening hard waters, are dealt with in elementary works (*College Course*, Chap. VI), and only a brief summary is given here.

Although *rain water* is natural distilled water it is far from pure, having taken up impurities in falling through the atmosphere: dissolved gases (oxygen, nitrogen, inert gases, carbon dioxide), salts (sodium chloride from sea-spray, sodium sulphate, etc.), nitrous and nitric acids from electrical discharges and their ammonium salts, and near towns free sulphuric acid from pyrites in coal fuel, and suspended soot. Snow contains similar impurities.

In percolating through the soil to form *river water* the rain water takes up from the soil salts, organic matter, and suspended matter, the dissolved carbonic acid (from CO_2 in the air and soil) forming soluble calcium and magnesium bicarbonates $Ca(HCO_3)_2$ and $Mg(HCO_3)_2$ from the normal carbonates in the soil. Calcium and magnesium sulphates and chlorides may also dissolve.

Thames water, flowing over soil rich in calcium carbonate, contains 157 mg. of $CaCO_3$ per lit. Trent water flowing over soil containing gypsum contains 300 mg. of $CaSO_4$ per lit.; whilst the rivers Dee and Don draining the Aberdeen granite area, Glasgow water from Loch Katrine, and Bala Lake water, are very soft.

Spring (or *deep well*) water is essentially river water which has undergone filtration.

The *hardness* of water is usually expressed as parts of $CaCO_3$ per 100,000, equivalent to the calcium and magnesium salts present, or in grains per gallon (parts per 70,000), when it is given in "degrees." A *soft* water has less than 10° (10 grains $CaCO_3$ per gallon), a *medium hard water* 10°–20°, a *hard* water 20°–30°, and a *very hard* water over 30°, of hardness.

Temporarily hard water contains bicarbonates of calcium and magnesium which decompose on boiling:

$$Ca(HCO_3)_2 = CaCO_3 + CO_2 + H_2O$$

It then deposits normal calcium carbonate (solubility 0·013 g. per lit.) as a "fur" in kettles and a "scale" in boilers. These waters can be softened by *Clark's process* (1841), in which so much lime water (or milk of lime) is added as will precipitate the calcium as carbonate and the magnesium as *hydroxide* (solubility 0·01 g. per lit.), since magnesium carbonate is too soluble (0·84 g. per lit.):

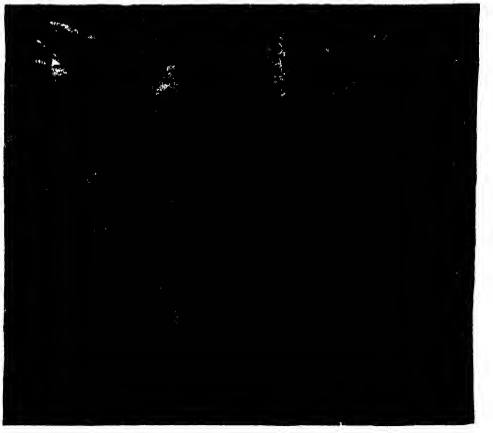
$$Ca(HCO_3)_2 + Ca(OH)_2 = 2CaCO_3 + 2H_2O$$
$$Mg(HCO_3)_2 + 2Ca(OH)_2 = Mg(OH)_2 + 2CaCO_3 + 2H_2O.$$

Natural water containing ferrous bicarbonate forms a brown precipitate of ferric hydroxide (in presence of oxygen) on boiling or exposure to air:

$$4Fe(HCO_3)_2 + O_2 + 2H_2O = 4Fe(OH)_3 + 8CO_2.$$

Water containing calcium and magnesium bicarbonates forms *stalactites* (on the roof) and *stalagmites* (on the floor) of carbonates on dripping from the roofs of caves (Fig. 284).

Permanently hard water (which may at the same time be temporarily hard) contains sulphates and chlorides of calcium and magnesium. On evaporation in boilers it precipitates a hard scale of anhydrous $CaSO_4$ (solubility 2 g. per litre, decreasing with rise of temperature almost to zero at boiler temperature), which causes overheating of the metal. Such water is softened by adding sodium carbonate: $CaSO_4 + Na_2CO_3 = CaCO_3 + Na_2SO_4$.



[*Photo. Frith & Co. Ltd.*

FIG. 284.—Stalactites and stalagmites.

If magnesium chloride is present it is precipitated as hydroxide by milk of lime (along with any calcium bicarbonate as carbonate) :

$$MgCl_2 + Ca(OH)_2 = Mg(OH)_2 + CaCl_2,$$

and the calcium chloride formed is then precipitated with sodium carbonate.

Hard waters cause loss of soap by precipitating the soap (sodium salts of fatty acids) as slimy calcium and magnesium salts, which carry down unchanged soap. About 0·17 lb. of soap is required for 100 gallons of water containing 1 grain of $CaCO_3$ per gallon (= 1 degree of hardness), instead of the theoretical 0·075 lb. ; or 17½ oz. of soap for 10 degrees, and 26 oz. for 15 degrees of hardness (Harwood, *J.S.C.I.*, 1941, **60**, 760).

Temporary and permanent hardness are now mostly removed by the *base-exchange* (or *zeolite*) *process*, in which the water is percolated through grains of a sodium aluminium silicate or zeolite (p. 426). The natural water-softening minerals are either glauconites, dark green or brown, sandy and practically non-porous, or else porous brick-like materials. The artificial zeolites (*e.g.* " permutit ") are porous gels precipitated by mixing solutions of sodium silicate and sodium aluminate.

The base exchange material may be formulated as Na_2Ze, where Ze is the " zeolite radical " ; Ze is often formulated as $Al_2H_4Si_3O_{12}$, but the commercial products contain more silica and approximate to $Na_2O,Al_2O_3,nSiO_2$ ($n = 5$ to 13). The calcium and magnesium ions in the water are exchanged for an equivalent of sodium ions in the zeolite, the anions remaining in solution :

$$Na_2Ze + Ca^{\cdot\cdot} \rightleftharpoons 2Na^{\cdot} + CaZe.$$

The change is reversible and when the zeolite ceases to function it is percolated with a solution of common salt, which displaces the calcium amd magnesium ions and replaces them by sodium, and calcium and magnesium chlorides pass into solution. There is a mass-action effect and in practice about 2½ times the theoretical amount of salt is used.

A zeolite containing manganese dioxide (regenerated by percolating with permanganate solution) oxidises dissolved iron and manganese salts (producing brown stains in laundries) and precipitates them as oxides.

A synthetic resin base-exchange material takes up calcium, magnesium and sodium ions, replacing them by hydrogen ions and forming a solution of carbonic acid. The material is regenerated by dilute sulphuric acid.

Waters are also softened on a smaller scale by adding sodium hexametaphosphate (p. 610) ; the calcium is not precipitated, but forms a complex ion which does not precipitate soap :

$$Na_2[Na_4(PO_3)_6] + CaSO_4 = Na_2[CaNa_2(PO_3)_6] + Na_2SO_4.$$

Hardness is not injurious to health and bicarbonates give the water a refreshing taste and prevent corrosion of lead pipes. Drinking water is softened to some extent, filtered through beds of gravel, and freely exposed to air so as to take up oxygen. It may be sterilised by ozone (p. 665), or by adding small quantities of chlorine, bleaching powder, or else chlorine and ammonia (*chloramine process*) which are more active than chlorine alone.

Some waters passing through iron pipes form growths of vegetation, which rapidly corrode the iron and in time the pipes may be choked. Lead is rapidly attacked by distilled or rain water in presence of air, forming lead hydroxide, which is appreciably soluble or forms a colloidal solution. The action is due partly to dissolved oxygen, and partly to *free* carbonic acid. Hard water has much less action on lead than soft water. Bicarbonates (temporary hardness) reduce the action on lead, free carbonic acid (*e.g.* in rain water) increases it. Peaty waters, containing organic acids, act rapidly on lead or zinc, unless neutralised by lime.

EXPT. 1.—Two pieces of clean lead pipe are placed in distilled water and tap-water in beakers, the metal being only partly covered. On standing the distilled water becomes turbid, whilst the tap-water (if hard) remains clear. Pour off the liquids and add hydrogen sulphide water. Compare the brown or black colorations (due to lead sulphide). The water should not be filtered, as dissolved lead hydroxide is retained to some extent by filter paper.

Sea water contains on the average 3·6 p.c. of dissolved solids, of which 2·6 p.c. is sodium chloride. The amount varies and often decreases with the depth: Baltic 0·3–0·8 p.c., Black Sea 1·8–2·2 p.c., Atlantic 3·3–3·7 p.c., Mediterranean 3·8–4·1 p.c., Caspian 12·7–28·5 p.c., Dead Sea 19·2–26 p.c., Elton Lake (Russia) 26·5 p.c. Sea water is usually faintly alkaline (pH about 8). An analysis of the Irish Sea in parts per 100,000 is:

NaCl	KCl	$MgCl_2$	$MgBr_2$	MgI_2	$MgSO_4$	$CaSO_4$	$CaCO_3$
26·44	0·746	3·151	0·0705	0·0025	2·066	1·332	0·0475

Mineral waters are natural waters containing special constituents not present (except in traces) in ordinary water. They are of several kinds:

(1) *Acidulous* (*e.g.* Apollinaris and Seltzer (*i.e.* Selters) waters), containing dissolved carbon dioxide, sometimes together with common salt. The carbon dioxide may be liberated with effervescence when the water is shaken or slightly warmed.

(2) *Alkaline* (*e.g.* Vichy water), containing sodium bicarbonate and sometimes lithium bicarbonate, which are supposed to be beneficial in the treatment of gout.

(3) *Bitter*, containing various salts. *E.g.* Marienbad water (sodium sulphate), Epsom water (magnesium sulphate), Friedrichshall and Hunyadi-Janos waters (sodium and magnesium sulphates).

(4) *Chalybeate* or *ferruginous* (*e.g.* Pyrmont water), containing ferrous bicarbonate.

(5) *Hepatic* (Latin *hepar*, liver), containing hydrogen sulphide and alkali sulphide, *e.g.* Na_2S. They smell of hydrogen sulphide and on exposure to air deposit sulphur: $2H_2S + O_2 = 2H_2O + 2S$. Harrogate water is of this type.

(6) *Siliceous*, containing dissolved silica and alkali silicates. Such waters, *e.g.* of the geysers of Iceland, New Zealand, and Yellowstone Park (America), are usually almost boiling and deposit masses of siliceous sinter at the mouth of the geyser.

(7) *Iodine*, containing dissolved iodides, at Woodhall Spa (Lincoln) and in Central Europe.

Hot springs in various places, *e.g.* Buxton (28°) and Bath (47°), contain dissolved gas, including helium, and often traces of radium emanation.

Dissociation of steam.—Although water is very stable, steam is slightly dissociated at high temperatures into its elements : $2H_2O \rightleftharpoons 2H_2 + O_2$. These recombine on cooling unless this is very rapid, when the velocity of recombination becomes negligible.

The thermal dissociation of steam was discovered by Grove (*Phil. Trans.*, 1847, **137**, 1), who heated a platinum wire electrically in steam, passed sparks through steam, and plunged the fused end of a platinum wire into water. In 1863 Deville poured more than a kilogram of fused platinum into water and found that detonating gas was freely evolved. By passing a stream of moist carbon dioxide through a porcelain tube heated at 1300° and absorbing the gas in potash, he obtained 25 c.c. of detonating gas in two hours.

Nernst and von Wartenberg (1906) passed steam containing some electrolytic gas through a strongly heated porcelain tube and collected the detonating gas, chilled by passing through a capillary, over mercury, the volume of liquid water condensed being also measured.

Löwenstein (1906) measured the density of steam in a strongly heated iridium bulb (p. 19) and also the pressure of hydrogen which permeated a vacuous palladium bulb strongly heated in steam. The heated platinum wire method was used by Langmuir (1906) and Holt (1907), and Siegel (1914) measured the pressure developed on the explosion of electrolytic gas, which is reduced by incomplete combination.

Nernst calculated the following percentage dissociations of steam :

$T°$ abs.	10 atm.	1 atm.	0·1 atm.	0·01 atm.
1000	$1·39 \times 10^{-5}$	$3·00 \times 10^{-5}$	$6·46 \times 10^{-5}$	$1·39 \times 10^{-4}$
1500	$1·03 \times 10^{-2}$	$2·21 \times 10^{-2}$	$4·76 \times 10^{-2}$	0·103
2000	0·273	0·588	1·26	2·70
2500	1·98	3·98	8·16	16·6

If p is the total pressure in atm. and x the degree of dissociation :

$$\frac{px^3}{(1-x)(2+x)} = K,$$

and

$$\log K = -26000/T + 6·06.$$

At high temperatures steam also dissociates into hydrogen and the hydroxyl radical : $2H_2O \rightleftharpoons H_2 + 2OH$; the following calculated percentage dissociations are at 1 atm. pressure :

$T°$ abs.	1500	2000	2500	3000
	0·014	0·59	5·6	26

The hydroxyl radical has been detected spectroscopically in flames and the electric discharge through steam. It has a short life, comparable with that of atomic hydrogen. When formed from steam it undergoes a surface reaction and forms atomic oxygen : $2OH = H_2O + O$.

Liquid water is decomposed by short-wave ultra-violet light or α-rays. At first only hydrogen is evolved and hydrogen peroxide formed : $2H_2O = H_2 + H_2O_2$, but after a time oxygen is also evolved : $2H_2O_2 = 2H_2O + O_2$.

Hydrogen Peroxide

Hydrogen peroxide was discovered by Thenard in 1818 by the action of acids on barium peroxide. He concentrated the solution by evaporation in a vacuum desiccator over concentrated sulphuric acid, and also by distillation under reduced pressure, and so obtained nearly pure hydrogen peroxide. By decomposing a weighed amount in a tube over mercury by heat or by the catalytic action of manganese dioxide, and measuring the oxygen evolved he deduced the empirical formula HO for the substance, which he called *oxygenated water*. He found that it is an oxidising agent, liberating iodine from potassium iodide.

Traces (4×10^{-10} g./lit.) of hydrogen peroxide vapour occur in the atmosphere (Schöne, 1893–4) ; H_2O_2 is found in rain and snow and in many natural waters, but is not formed by the spontaneous evaporation of water in air. According to Bach (1894, 1902) it is present in traces in green plants, but this has been denied.

Hydrogen peroxide is formed when a hydrogen or carbon monoxide flame is allowed to play on the surface of cold water, ice or solid carbon dioxide (Traube, *Ber.*, 1885, **18**, 1894).

EXPT. 2.—Allow a hydrogen flame to impinge on a piece of ice. Pour out the water formed and add a little titanyl sulphate solution made by heating TiO_2 with twice its volume of concentrated sulphuric acid, cooling and diluting with cold water. A yellow colour indicates the presence of H_2O_2.

Traces of hydrogen peroxide are formed by passing a mixture of hydrogen and oxygen over palladium black : $H_2 + O_2 = H_2O_2$. Small amounts are also formed by the action of bright sunlight, ultra-violet light, or radium emanation on water containing dissolved oxygen ; or by the action of a brush discharge on a mixture of steam and oxygen, $2H_2O + O_2 = 2H_2O_2$, or on a non-explosive mixture of hydrogen and oxygen at $-80°$, or the mixture $H_2 + O_2$ at 3 cm. pressure.

Hydrogen peroxide is formed by the action of acids on metal *peroxides* containing the —O—O— group (p. 656). To obtain it free from soluble salts, barium peroxide may be used with an acid such as sulphuric, carbonic, phosphoric or hydrofluosilicic (H_2SiF_6) which forms an insoluble barium salt, or potassium peroxide with a concentrated solution of tartaric acid when potassium hydrogen tartrate is precipitated. The filtrate is an aqueous solution of hydrogen peroxide.

EXPT. 3.—Stir barium peroxide with distilled water and pass carbon dioxide into the suspension. After a few minutes add a solution of potassium iodide and starch : a blue colour is produced : $BaO_2 + CO_2 + H_2O = BaCO_3 + H_2O_2$. According to Merck unstable barium percarbonate $BaCO_4$ is first produced, and then hydrolysed :

$$BaO_2 + CO_2 = BaCO_4 ; \quad BaCO_4 + H_2O = BaCO_3 + H_2O_2.$$

Anhydrous barium peroxide is not easily decomposed by dilute sulphuric acid, since insoluble sulphate deposits on the particles. A *hydrated* barium peroxide $BaO_2,8H_2O$ is readily decomposed and is prepared by stirring the peroxide with water and allowing to stand, or pure by the following method.

Commercial barium peroxide is finely powdered and added a little at a time to a cold mixture of equal volumes of water and concentrated hydrochloric acid until the acid is neutralised. A little baryta solution is added to precipitate iron and aluminium as hydroxides. These, with any silica contained in the barium peroxide, are filtered off and the filtrate added to saturated baryta water. A white crystalline precipitate of $BaO_2,8H_2O$ is formed, which is filtered off, washed with cold water free from carbon dioxide, and kept moist in a stoppered bottle :

$$BaO_2 + 2HCl = BaCl_2 + H_2O_2$$
$$H_2O_2 + Ba(OH)_2 + 6H_2O = BaO_2,8H_2O.$$

If the hydrated peroxide is added to cold dilute sulphuric acid (1 vol. acid : 5 vols. H_2O) or hydrofluosilicic acid, insoluble barium salts and a solution of hydrogen peroxide are formed :

$$BaO_2 + H_2SO_4 = BaSO_4 + H_2O_2$$
$$BaO_2 + H_2SiF_6 = BaSiF_6 + H_2O_2.$$

Hydrogen peroxide is more stable in acid solution and the commercial substance contains a little free acid, *e.g.* sulphuric.

Sodium peroxide added in small quantities at a time to 20 p.c. sulphuric acid cooled in ice reacts : $Na_2O_2 + H_2SO_4 = Na_2SO_4 + H_2O_2$. Two-thirds of the sodium sulphate separate as Glauber's salt $Na_2SO_4,10H_2O$, and the liquid is decanted and distilled in vacuum (Kilpatrick, etc., *J.A.C.S.*, 1926, **48**, 3019).

Hydrogen peroxide is now largely manufactured by an *electrolytic process* ; 50 p.c. sulphuric acid is electrolysed, and the resulting solution containing persulphuric acid distilled in a vacuum in a special apparatus, *e.g.* a lead spiral, in which the vapour is rapidly separated. In this way pure 30 p.c. H_2O_2 solution is obtained :

$$2H_2SO_4 = H_2S_2O_8 + H_2 \quad \text{electrolysis}$$
$$\left.\begin{aligned} H_2S_2O_8 + H_2O &= H_2SO_5 + H_2SO_4 \\ H_2SO_5 + H_2O &= H_2SO_4 + H_2O_2. \end{aligned}\right\} \text{hydrolysis}$$

Dilute solutions of hydrogen peroxide are used in pharmacy. The strength is stated in terms of the volume of oxygen evolved on heating 1 vol. of peroxide : $2H_2O_2 = 2H_2O + O_2$. Commercial peroxide is usually " 10 volumes," or " 20 volumes." The 30 p.c. preparation evolves 100 volumes of oxygen. From the equation it is seen that each g. of peroxide evolves 329·4 c.c. of O_2 at S.T.P. A 1 p.c. solution evolves 3·294 times its volume of oxygen and the " 10 vol. " peroxide contains 3·04 p.c. of H_2O_2.

Dilute hydrogen peroxide may be concentrated to 66·6 p.c. by evaporation in a dish on a water bath at 75°, as H_2O_2 is less volatile than water, or to 30 p.c. by distilling with xylene and then to 90 p.c. by distilling with *p*-cymene (Hurd

and Puterbaugh, *J.A.C.S.*, 1930, **52**, 950), water distilling over with these immiscible liquids (p. 61). By evaporating over concentrated sulphuric acid in a vacuum desiccator cooled in a freezing mixture Thenard obtained 95 p.c. H_2O_2, density 1·452, evolving 475 vols. of oxygen ; he also concentrated the peroxide by distillation under reduced pressure, water being more volatile, and this method was used by Wolffenstein in 1894 to obtain nearly pure hydrogen peroxide. He found that the fraction coming over at 81°–85° at 65 mm. contained 90·5 p.c. H_2O_2 and by redistilling this the fraction at 84°–85° was 99·1 p.c. H_2O_2.

The apparatus shown in Fig. 285 may be used, technical 100 vol. (30 p.c.) peroxide being the starting material (Brühl, *Ber.*, 1895, **28**, 2847 ; Maass, etc., *J.A.C.S.*, 1920, **42**, 2548).

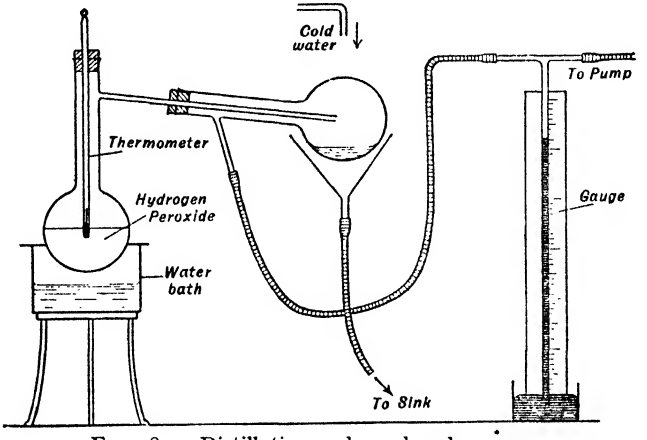


FIG. 285.—Distillation under reduced pressure.

Pure hydrogen peroxide is a clear syrupy liquid, s. g. 1·4694 at 0°, colourless in small amounts but bluish like water when in bulk. It smells like nitric acid, has a harsh metallic taste, and blisters the skin. It evaporates spontaneously in air, b.p. 84°–85°/68 mm. and 69·2°/26 mm. ; when heated to 151°, the b.p. at 760 mm., it explodes. It is diamagnetic. The pure liquid has a strong acid reaction, but dilute solutions are neutral.

Pure hydrogen peroxide is fairly stable and can be kept for several weeks in absence of sunlight in a smooth glass bottle, but in contact with rough surfaces or on shaking it decomposes. Finely divided gold, silver and platinum (but not iron) cause explosive decomposition. Cotton wool, or a mixture of magnesium or carbon powder with a trace of manganese dioxide, inflames in contact with the pure liquid.

On cooling 95–96 p.c. hydrogen peroxide in solid carbon dioxide and ether, or methyl chloride at −23°, it solidifies to hard crystals, and if a little of the solid is placed in 95 p.c. solution cooled at −10°, pure solid hydrogen peroxide separates in tetragonal prisms, m.p. −0·89° (Maass, etc., *J.A.C.S.*, 1928, **50**,

1120). These explode in contact with platinum black. On cooling a solution in solid carbon dioxide and ether a crystalline hydrate $H_2O_2,2H_2O$, m.p. $-51°$, is formed, but water and hydrogen peroxide form solid solutions (Giguère and Maass, *Canad. J. Res.*, 1940, **18**, 66).

The *reactions of hydrogen peroxide* may be divided into (i) catalytic decomposition, (ii) addition reactions, (iii) oxidising reactions, (iv) reducing reactions.

Catalytic reactions of hydrogen peroxide.—Although hydrogen peroxide is exothermic when formed from the *elements*: $H_2 + O_2 = H_2O_2 + 45{\cdot}2$ k. cal., it decomposes into liquid *water* and oxygen with evolution of heat: $H_2O_2 = H_2O + \frac{1}{2}O_2 + 23{\cdot}0$ k. cal., and the pure substance may explode in undergoing this change. The solutions decompose spontaneously with evolution of oxygen in presence of traces of alkali, but are stabilised by traces of acids, alcohol, glycerol or barbituric acid. Traces of dust accelerate the decomposition and a pure dust-free 50 p.c. solution is stable for a long time in a silica vessel (Rice, *J.A.C.S.*, 1926, **48**, 2099).

Platinum black and especially colloidal platinum, manganese dioxide, finely divided silver, and a solution of osmium tetroxide, are active catalysts.

Liebermann (1904) considered that platinum first absorbs atmospheric oxygen and the activated oxygen, probably atomic, reacts with a labile oxygen atom of the hydrogen peroxide: $H_2O_2 + O - H_2O + O_2$.

Addition compounds of hydrogen peroxide.—Hydrogen peroxide forms compounds with some organic substances and salts: $(NH_4)_2SO_4,H_2O_2$, $K_2CO_3,2H_2O_2$, Na_2HPO_4,H_2O_2, in which it shows analogies with water of crystallisation. The crystalline compound with urea CON_2H_4,H_2O_2, stabilised by a trace of citric acid, is called *hyperol*: it liberates hydrogen peroxide when dissolved in water. The crystalline compound $(NH_4)_2SO_4,H_2O_2$, obtained from 30 p.c. hydrogen peroxide and ammonium sulphate, gives very concentrated hydrogen peroxide when distilled in vacuum. With ammonia hydrogen peroxide forms the compounds NH_3,H_2O_2 and $2NH_3,H_2O_2$, which may be formulated as $NH_4{\cdot}O_2H$ (ammonium hydrogen peroxide) and $(NH_4)_2O_2$ (ammonium peroxide).

Oxidising reactions of hydrogen peroxide.—Hydrogen peroxide, with a labile oxygen atom: $H_2O_2 = H_2O + O$, is an *active oxidising agent*. Arsenious and sulphurous acids are oxidised to arsenic and sulphuric acids: $H_3AsO_3 + H_2O_2 = H_3AsO_4 + H_2O$; $H_2SO_3 + H_2O_2 = H_2SO_4 + H_2O$. Black lead sulphide is oxidised to white lead sulphate: $PbS + 4H_2O_2 = PbSO_4 + 4H_2O$, a reaction used in restoring discoloured oil-paintings in which the white-lead pigment (basic lead carbonate) has been partly converted into black PbS by atmospheric hydrogen sulphide. Ferrous salts in acid solution are converted into ferric salts: $2FeSO_4 + H_2O_2 + H_2SO_4 = Fe_2(SO_4)_3 + 2H_2O$. Iodine is liberated rather slowly from potassium iodide, but rapidly in presence of a little ferrous sulphate: $2KI + H_2O_2 = 2KOH + I_2$. In acid solution the reaction is: $2KI + H_2O_2 + H_2SO_4 = K_2SO_4 + 2H_2O + I_2$.

The oxidising action of hydrogen peroxide is used in *bleaching* delicate materials (wool, silk, ivory, feathers) which would be injured by chlorine: the

solution is made faintly alkaline with ammonia or added to 10 p.c. sodium acetate solution. Hydrogen peroxide bleaches hair to a golden-yellow colour. It is also an antiseptic, and as it leaves no injurious products it is used as a gargle, etc.

Reducing reactions of hydrogen peroxide.—In some cases hydrogen peroxide acts as a reducing agent. Thenard (1819) found that gold and silver oxides are reduced to the metals : $H_2O_2 + Ag_2O = H_2O + O_2 + 2Ag$.

EXPT. 4.—Add NaOH solution to $AgNO_3$ solution, when a *brown* precipitate of silver oxide is formed. Add H_2O_2 solution. The precipitate is at once converted into *black* metallic silver, with brisk evolution of oxygen. A further quantity of H_2O_2 is *catalytically* decomposed by the finely divided silver.

Brodie (*Phil. Trans.*, 1850, **140**, 759 ; 1863, **152**, 837) found that when hydrogen peroxide acts as a reducing agent, the labile oxygen atom withdraws another oxygen atom from the compound reduced, so as to form an oxygen molecule O_2.

Hydrogen peroxide is used as an *antichlor* to remove excess of chlorine from bleached fabrics : $Cl_2 + H_2O_2 = 2HCl + O_2$. A solution of potassium permanganate acidified with sulphuric acid is readily reduced by hydrogen peroxide with evolution of oxygen (p. 651) :

$$2MnO_4' + 5H_2O_2 + 6H^{\cdot} = 2Mn^{\cdot\cdot} + 8H_2O + 5O_2.$$

Manganese dioxide is reduced in *acid* solution to a manganous salt :

$$MnO_2 + H_2O_2 + H_2SO_4 = MnSO_4 + 2H_2O + O_2.$$

Solutions of bleaching powder and sodium hypobromite evolve oxygen : $NaOBr + H_2O_2 = NaBr + H_2O + O_2$. Titration with permanganate, and measurement of the oxygen evolved with hypobromite, are used in the *determination* of H_2O_2 ; for traces, the colour reaction (p. 679) with titanyl sulphate solution is used.

Brodie found that in acid solution, ferrocyanide is oxidised to ferricyanide :

$$2Fe(CN)_6'''' + H_2O_2 + 2H^{\cdot} = 2Fe(CN)_6''' + 2H_2O,$$

whilst in alkaline solution ferricyanide is reduced to ferrocyanide :

$$2Fe(CN)_6''' + H_2O_2 + 2OH' = 2Fe(CN)_6'''' + 2H_2O + O_2.$$

Tests for hydrogen peroxide.—Hydrogen peroxide, even at a dilution of 1 pt. in 25 millions, liberates iodine from an iodide solution, giving a blue colour with starch, but ozone, halogens, and nitrites also give this reaction. Hydrogen peroxide acts powerfully on a photographic plate.

A delicate test is the formation of blue *perchromic acid*, soluble in ether, with chromic acid solution.

EXPT. 5.—A dilute solution of potassium dichromate acidified with sulphuric acid is added to very dilute hydrogen peroxide in a stoppered cylinder, a layer of ether is poured on, and the cylinder shaken. The ether floats to the surface with a deep blue colour due to perchromic acid. On standing for some time,

this colour fades and a green solution of a chromic salt is formed in the lower layer. The test is masked by vanadium compounds, unless sodium phosphate is added.

The most delicate test is the formation of a yellow colour due to *pertitanic acid* with a solution of titanyl sulphate (p. 679).

Other tests for hydrogen peroxide are: (1) guiacol solution acidified with sulphuric acid gives a blue colour; (2) guiacum tincture with a little blood or malt extract gives a blue colour (also a test for blood-stains); (3) a solution of aniline and potassium chlorate in dilute sulphuric acid gives a violet colour; (4) filter paper soaked in cobalt naphthenate and dried changes from rose colour to olive-green.

The formula of hydrogen peroxide.—The vapour density of hydrogen peroxide at 90° (Maass, etc., *J.A.C.S.*, 1929, **51**, 674) and the freezing point of its aqueous solution (Carrara, 1892), correspond with the formula H_2O_2. In the pure state hydrogen peroxide is probably associated, with hydrogen bonds, like water.

The simplest constitutional formula is H·O·O·H, *i.e. dihydroxyl*, which would agree with the general instability of compounds containing chains of oxygen atoms. To account for the instability of one oxygen atom, Buff (1866) and Kingzett (1882) assumed that one oxygen is quadrivalent, O=O=H_2, and Brühl (1895) from the molecular dispersion concluded that both oxygens are quadrivalent, HO≡OH. In modern valency theory the formula could be written [O=O→H]′H˙, as a weak acid: the dissociation constant at 25° is $[H^{\cdot}][HO_2']/[H_2O_2] = 1{\cdot}55 \times 10^{-12}$ (Kargin, 1929).

Baeyer and Villiger (*Ber.*, 1900, **33**, 3387) by the action of 12 p.c. hydrogen peroxide and alkali on diethyl sulphate $(C_2H_5)_2SO_4$ obtained explosive *ethyl hydroperoxide* $C_2H_5HO_2$ and stable *diethyl peroxide* $(C_2H_5)_2O_2$, b.p 65°. Zinc and acetic acid reduce diethyl peroxide to alcohol, C_2H_5OH, which supports the formula $C_2H_5{\cdot}O{\cdot}O{\cdot}C_2H_5$, as with 2H this gives $2C_2H_5OH$. The formula $O{=}O(C_2H_5)_2$ would suggest that ether $O(C_2H_5)_2$ should be formed on reduction. If diethyl peroxide is $C_2H_5{\cdot}O{\cdot}O{\cdot}C_2H_5$, hydrogen peroxide is probably H·O·O·H.

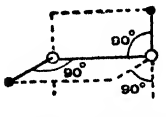


FIG. 286.—Structure of hydrogen peroxide.

The X-ray spectrum of pure liquid H_2O_2 shows that the two hydrogen atoms are fixed in two directions perpendicular to one another and to the axis joining the two oxygen atoms (Fig. 286) (Randall, *Proc. Roy. Soc.*, 1937, **159**, 83).

By streaming oxygen and atomic hydrogen through a bulb cooled in liquid air a glassy condensate is formed which at −115° decomposes with evolution of oxygen and formation of ordinary hydrogen peroxide. This is regarded (Geib and Harteck, 1932) as an isomeric form $H_2{=}O{\rightarrow}O$.

True *peroxides* (or *superoxides*) such as H·O·O·H, Na·O·O·Na and Ba  contain the *peroxide radical* —O—O—. With dilute acids they form hydrogen

peroxide. The *dioxides* of some metals functioning with higher valency, such as PbO_2 or O=Pb=O and O=Mn=O, do not form H_2O_2 with dilute acids; on warming with concentrated hydrochloric acid they evolve chlorine, first forming unstable $PbCl_4$, etc. Brodie (1863) found, however, that barium peroxide evolves chlorine with *concentrated* hydrochloric acid:

$$BaO_2 + 4HCl = BaCl_2 + Cl_2 + 2H_2O.$$

Autoxidation.—The formation of hydrogen peroxide in the slow oxidation of turpentine, phosphorus and metals by gaseous oxygen in presence of water was called *autoxidation* by Schönbein in 1858.

EXPT. 6.—Add a little turpentine to dilute potassium iodide solution and starch solution in an open flask, shake, and allow to stand. A blue colour develops.

Schönbein found that the oxygen absorbed is shared equally between the substance oxidised, *e.g.* lead, and the water. He supposed that *atomic* oxygen exists in two forms, negative *ozone* ⊖ and positive *antozone* ⊕. The antozone formed hydrogen peroxide with water, or oxidised indigo solution or other oxidisable substance present. Brodie showed that all the supposed reactions of antozone are due to hydrogen peroxide.

Brodie (1850) and Clausius (1858) supposed that the oxygen *molecule*, which they regarded as composed of two atoms of opposite polarities, is divided in autoxidation reactions, one atom oxidising a substance and the other forming H_2O_2 with a molecule of water: $Pb + O_2 + H_2O = PbO + H_2O_2$.

M. Traube (1882) suggested that the oxygen molecule as a whole unites with an oxidisable substance to form a *holoxide* or *moloxide*, and in autoxidation it takes H_2 from water to form H_2O_2, the oxygen atom in water oxidising the other substance. In the combustion of hydrogen, H_2O_2 was supposed to be a primary product: $H_2 + O_2 = H_2O_2$, and in the combustion of carbon monoxide the reaction was supposed to be:

$$CO + OH_2 + O_2 = CO_2 + H_2O_2; \quad CO + H_2O_2 = CO_2 + H_2O.$$

The autoxidation reaction with zinc, water and oxygen he represented as:

$$Zn + O\,\vdots\,H_2 + O_2 = ZnO + H_2O_2.$$

Bach (1897) concluded that a substance undergoing autoxidation (*autoxidiser* A) combines with an oxygen molecule to form an unstable peroxide: $A + O_2 = AO_2$. This may react with water to form the lower oxide and drogen peroxide:

$$AO_2 + H_2O = AO + H_2O_2$$

or with some other *acceptor* B to form an oxide BO:

$$AO_2 + B = AO + BO.$$

He represented the combustion of carbon monoxide by the scheme:

$$CO + O_2 = O : C : O_2; \quad O : C : O_2 + CO = 2CO_2.$$

The unstable higher oxides of metals supposed to be formed in autoxidation reactions, ZnO_2, PbO_2, etc., are not the known ones, which do not give hydrogen peroxide with water, but much more labile compounds:

$$Zn + O_2 = ZnO_2; \quad ZnO_2 + H_2O = ZnO + H_2O_2.$$

Engler and Wild (*Ber.*, 1897, **30**, 1669) modified Bach's theory by supposing that the oxygen molecule is first "opened out" to form —O—O— which combines with the *activator* such as turpentine to form an unstable peroxide. (Turpentine forms a peroxide on standing in a loosely stoppered bottle and its bleaching and disinfecting properties are due to its ability to activate oxygen.)

Induced oxidation.—A solution of sodium arsenite Na_3AsO_3 is not oxidised to arsenate Na_3AsO_4 on exposure to air, but a solution of sodium sulphite Na_2SO_3 is oxidised to sulphate Na_2SO_4. If the two solutions are mixed and exposed to air, both the sulphite and arsenite are oxidised.

$$Na_2SO_3 + Na_3AsO_3 + O_2 = Na_2SO_4 + Na_3AsO_4.$$

This is an example of an *induced reaction*, several examples of which were collected by Kessler in 1861–63. They may be explained either by Brodie's or Bach's theory. The sulphite is called the *inductor*, the oxygen molecule the *actor*, and the arsenite the *acceptor*:

I. *Brodie's theory*: $Na_2SO_3 + O_2 + H_2O = Na_2SO_4 + H_2O_2$

$Na_3AsO_3 + H_2O_2 = Na_3AsO_4 + H_2O.$

II. *Bach's theory*: $Na_2SO_3 + O_2 = Na_2SO_5$

$Na_2SO_5 + Na_3AsO_3 = Na_2SO_4 + Na_3AsO_4.$

Deuterium peroxide.—A "heavy" hydrogen peroxide, *deuterium peroxide* D_2O_2, is formed by passing "heavy steam" (D_2O vapour) through a mixture of deuterosulphuric acid D_2SO_4 and potassium persulphate $K_2S_2O_8$ (which form D_2SO_5, undergoing hydrolysis by D_2O; see p. 680) and condensing the vapour. The solution of D_2O_2 in D_2O thus obtained is fractionated, and pure D_2O_2 obtained (Feher, 1939). HDO_2 is also known.

CHAPTER XXIV

SULPHUR

THE elements sulphur, selenium and tellurium form a distinct group which stands somewhat apart from oxygen, the first member of Group VI (see p. 647).

Sulphur was known in antiquity; the Greek name θεῖον has provided the prefix *thio* for a number of its compounds. The alchemists regarded it as the principle of combustibility but it was later considered to be a compound of phlogiston and sulphuric acid. Its elementary character was recognised by Lavoisier in 1777.

Free sulphur occurs in large quantities in Sicily and in the southern States of Louisiana and Texas in America. Smaller amounts occur in New Zealand, Chile, Russia, Iceland and especially Japan.

The sulphur in Sicily may have been formed by the reduction of calcium sulphate by organic matter and bacteria, which would account for the calcium carbonate found with it (cf. Elion, *Ind. Eng. Chem.*, 1927, **19**, 1368):

$$2CaSO_4 + 3C = 2CaCO_3 + 2S + CO_2.$$

It occurs mostly with gypsum, celestine ($SrSO_4$) and limestone, sometimes in large rhombic crystals but usually in yellow or grey crystalline masses. Fused sulphur usually deposits monoclinic crystals, but rhombic crystals may deposit on very slow cooling of large masses of liquid. The sulphur in the craters of extinct volcanoes, *e.g.* in Japan and Mexico, may have been formed by the interaction of hydrogen sulphide and sulphur dioxide:

$$2H_2S + SO_2 = 2H_2O + 3S,$$

but this reaction usually occurs only in solution (Cluzel, 1812; Matthews, *J.C.S.*, 1926, 2270) and thionic acids (p. 727) are also formed. The reverse reaction occurs slowly when sulphur is boiled with water.

EXPT. 1.—Invert a dry jar of sulphur dioxide over one of hydrogen sulphide and remove the plates. No action occurs. Add water and shake. Yellow sulphur is deposited.

Sulphur is formed, probably by this reaction, in hot springs in Iceland, Wyoming, California and Utah, and in *solfotara*, or vents evolving sulphurous gases and steam in volcanic districts.

Combined sulphur occurs as metal sulphides such as galena (PbS), blende (ZnS), copper pyrites ($CuFeS_2$) and iron pyrites (FeS_2). Hydrogen sulphide occurs in volcanic gases and in some mineral springs, and sulphur dioxide in volcanic gases. Some springs and rivers (*e.g.* the Rio Vinagre in South America) contain free sulphuric acid. Large masses of gypsum are common. Sulphur occurs in some kinds of organic matter (onions, garlic, horse-radish, mustard, hair and wool), and the blackening of silver spoons by eggs is due to

sulphur compounds. Some bacteria (*e.g. Beggiatoa alba*) decompose sulphur compounds in their life processes, with separation of free sulphur.

Native sulphur in Sicily contains 15 to 25 p.c. S. It is stacked into heaps called *calcaroni*, built on a sloping hillside, with air spaces, and covered with powdered ore (Fig. 287). The ore is kindled at the top and the heat of combustion of about 30 p.c. of the sulphur melts the rest, which flows into wooden moulds. The blocks of crude sulphur contain 3–5 p.c. of rock and must be refined by distillation.

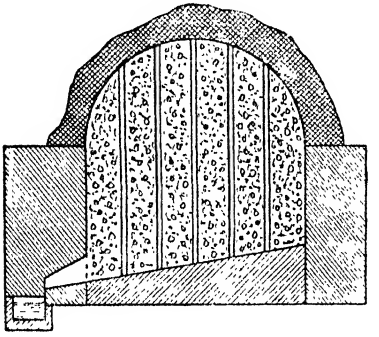


FIG. 287.—Sulphur kiln.

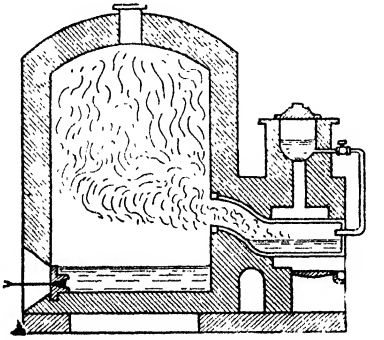


FIG. 288.—Refining of sulphur.

An improved method of extraction uses the *Gill kiln* (1880), a closed brick chamber with six compartments in a circle. The hot gas from one cell passes into an adjoining cell, and about 75 p.c. of the sulphur is recovered.

The crude sulphur is *refined* with the apparatus shown in Fig. 288. The sulphur fused in an iron pot flows into an iron retort. It boils and the vapour enters a large brickwork chamber, where it condenses on the cold walls as a light yellow powder called *flowers of sulphur*. As the walls become hot this melts (unless removed) and liquid collects at the bottom, whence it is tapped into cylindrical moulds to form *roll sulphur* or *brimstone*.

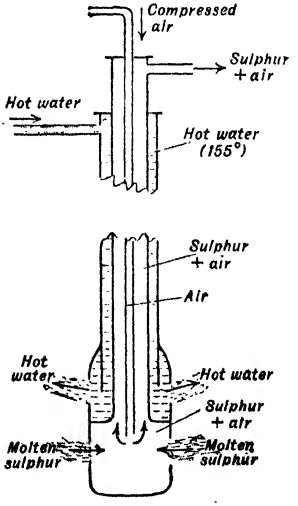


FIG. 289.—Frasch sulphur pump.

The *Frasch process* used in America is different. The deposit occurs below clay, quicksand and rock. A boring is made to the deposit and concentric pipes are sunk (Fig. 289). Down the outer pipe superheated water (155°) is pumped, which fuses the sulphur. Air is forced down the inner pipe, when an emulsion of molten sulphur and air-bubbles rises to the surface through the remaining annular space. This passes to large wooden vats, where the sulphur of 99·5 p.c. purity solidifies and is ready for immediate use. It contains a little petroleum which interferes with many experiments.

The extraction of sulphur from *alkali waste* (p. 306) containing calcium sulphide, by the *Chance process* (*J.S.C.I.*, 1888, **7**, 162), is obsolete. A suspension of the waste was decomposed by limekiln gas (containing carbon dioxide) to form hydrogen sulphide :

$$CaS + CO_2 + H_2O = CaCO_3 + H_2S$$
$$CaS + H_2S = Ca(SH)_2$$
$$Ca(SH)_2 + CO_2 + H_2O = CaCO_3 + 2H_2S,$$

and the gas mixed with air passed through a *Claus kiln* containing porous ferric oxide as a catalyst :

$$2H_2S + O_2 = 2H_2O + 2S.$$

The sulphur made by this process was very pure. The sulphur in *spent oxide* of gasworks (p. 458) is mostly burnt to make sulphuric acid.

Sulphur is recovered (Applebey, *J.S.C.I.*, 1934, **53**, 1097 R.) by absorbing the sulphur dioxide from roaster and smelter gases in a solution of sodium sulphite and aluminium chloride. On heating, the aluminium chloride hydrolyses, and the acid sulphite decomposes with evolution of sulphur dioxide, the reaction being reversed on cooling :

$$Na_2SO_3 + SO_2 + H_2O \rightleftharpoons 2NaHSO_3.$$

The sulphur dioxide is then reduced by passing over coke at 1100° :

$$SO_2 + C = CO_2 + S.$$

Crude sulphur is used for making sulphur dioxide and thence sulphuric acid, bisulphites for paper manufacture, and carbon disulphide. *Refined sulphur* is used in medicine, in powder form as a fungicide, as an insulator, and in the preparation of gunpowder, matches, fireworks and dyes. Sulphur is used in large quantities for *vulcanising* rubber.

For dressing vines to prevent the growth of the fungus *Oidium* (*Ind. Eng. Chem.*, 1929, **21**, 44, 359) sulphur is finely ground between millstones and sieved through silk (170 meshes to the inch). By blowing a current of air through the mill, the finest particles (" winnowed sulphur ") are carried off, and are retained by cloth filters.

Sulphur may be *purified* by repeated distillation in a current of pure carbon dioxide (Partington and Vogel, *J.C.S.*, 1925, **127**, 1514). The trace of residual hydrogen is removed by heating the vapour with S_2Cl_2 at 450° and removing S_2Cl_2 and HCl from the product in vacuum. This pure sulphur could be distilled unchanged in oxygen dried over P_2O_5 (Baker, 1888).

Allotropic Forms of Sulphur

Many allotropic forms of sulphur, crystalline and amorphous, are described. The best known are the two crystalline forms *rhombic* (α) and *monoclinic* (β), and the amorphous *plastic* sulphur.

(i) **Rhombic** (incorrectly called " octahedral "), S_α or S_I, axial ratios $a : b : c = 0{\cdot}8138 : 1 : 1{\cdot}9051$, s. g. 2·06, m.p. 112·8° (usually 110·2° owing to the presence of some S_π), soluble in CS_2, mol. wt. as vapour and in solution S_8.

(ii) **Monoclinic** (sometimes called " prismatic "), in different forms :

(*a*) common, S_β or S_{II}, axial ratios $a : b : c = 1{\cdot}99575 : 1 : 0{\cdot}99983$, angle $\beta = 84° 14'$, s. g. 1·96, m.p. 118·75° (usually 114·5° owing to the presence of some S_π), soluble in CS_2, mol. wt. as vapour and in solution S_8 ;

(*b*) *nacreous*, S_{III} (Gernez, 1883), axial ratios $a : b : c = 1{\cdot}06094 : 1 : 0{\cdot}70944$, angle $\beta = 88° 13'$, m.p. 106·8° ;

(*c*) S_{IV} (Muthmann, 1890).

(iii) **Rhombohedral** S_ϕ (Engel) or S_ρ (Aten), s. g. 2·135, soluble in CS_2, mol. wt. S_6.

(iv) **Amorphous** : (*a*) *plastic* S_γ, s. g. 1·92, a mixture of S_λ soluble in CS_2 and S_μ insoluble in CS_2 ; (*b*) *white*, found in flowers of sulphur, insoluble in CS_2, perhaps the same as S_μ ; (*c*) S_π (Magnus, 1856 ; Aten, 1912), deep yellow, soluble in CS_2, mol. wt. S_4 ; (*d*) precipitated (*milk of sulphur*), some varieties soluble (S_λ) and some insoluble (S_μ) in CS_2 (Berthelot, 1857).

(v) **Colloidal**, or S_δ.

Crystalline sulphur.—The common crystalline form, **rhombic** or **α-sulphur**, is prepared by allowing a solution of sulphur in carbon disulphide to evaporate in a loosely-covered dish at room temperature, when pale-yellow transparent crystals (Fig. 290) are formed, giving a lemon-yellow powder. It is insoluble in water, slightly soluble in alcohol and ether, freely soluble in carbon disulphide (1 in 3·5 CS_2 at 15°), sulphur chloride (S_2Cl_2), and hot benzene and turpentine. *Rhombic sulphur is the stable form at the ordinary temperature and most other forms pass into it on standing.* Roll sulphur is almost entirely rhombic sulphur, flowers of sulphur contain 70 p.c. of it, but when genuine also contain a yellowish-white amorphous variety (*white sulphur*) insoluble in carbon disulphide.

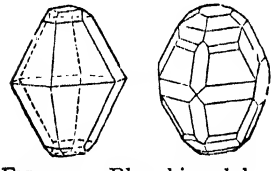


FIG. 290.—Rhombic sulphur.

X-rays show that the S_α crystals contain S_8 molecules (also present in the vapour and in solution) consisting of zig-zag octagonal rings (Fig. 291), with sixteen S_8 molecules in the unit cell of the crystal (Warren and Burwell, *J. Chem. Phys.*, 1935, **3**, 6).

FIG. 291.—Structure of S_8 molecule.

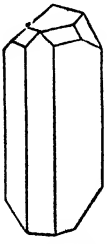


FIG. 292.—Monoclinic sulphur.

Monoclinic (" prismatic ") or **β-sulphur**, S_{II}, described by Mitscherlich in 1823, crystallises from fused sulphur or from solution in hot turpentine (Fig. 292). It is formed from α-sulphur above the transition temperature 95·5° : $S_\alpha \rightleftharpoons S_\beta$, and is metastable at room temperature (p. 53).

EXPT. 2.—Half fill a large porcelain crucible with small pieces of Sicilian roll sulphur (American sulphur gives a dark coloured product) and heat *gently* on a sand-bath till the whole is liquid. Allow to cool until a crust forms on the surface. Make two holes in this (one to admit air), and pour the liquid into a dry porcelain dish. Remove the

crust. The inside of the crucible is lined with transparent amber-yellow needles of β-sulphur. (The colour may be partly due to S_π, as crystals from solution are much paler.) On standing for a few days they become opaque, brittle, and lemon-yellow aggregates of minute crystals of α-sulphur, although the original monoclinic form is preserved and the crystal is a *pseudomorph*. The transition is readily followed by the colour.

β-Sulphur is insoluble in water but soluble in carbon disulphide; the solution on evaporation deposits α-sulphur. Crystals of β-sulphur slowly change at room temperature into minute crystals of α-sulphur and become opaque. Crystals of α-sulphur above 96° (more accurately 95·5°), especially at 110°, slowly form opaque aggregates of minute crystals of β-sulphur. The transformation is reversible: $S_\alpha \rightleftharpoons S_\beta$; below 96° S_α is stable, above 96° S_β. Below 0° the velocity of transition is so slow that β-sulphur remains unchanged for a very long time. Unlike iodine monochloride (p. 816), which is *monotropic*, only one form being stable at all temperatures, sulphur can exist in two forms with a transition temperature, and is *enantiotropic*.

The other monoclinic forms of sulphur are monotropic and have slightly different crystal angles.

S_{III} or *nacreous sulphur* (Gernez, 1883) is found native in oxidised pyrites and is obtained in pearly crystals by (*a*) cooling hot solutions of rhombic sulphur in toluene, alcohol, benzene, etc.; (*b*) cooling sulphur fused at 160° in a tube to 98° and scratching the inside of the tube with a platinum wire; (*c*) precipitating with ether a solution of sulphur in carbon disulphide; and (*d*) atmospheric oxidation of a solution of sulphur in alcoholic ammonium sulphide. S_{IV}, said to be formed in the last process at lower temperatures (Muthmann, 1890), is very unstable.

S_ϕ or S_ρ (Engel, 1891) is rhombohedral. It is prepared (Aten, *Z. phys. Chem.*, 1914, **88**, 321) by adding 150 c.c. of saturated sodium thiosulphate solution to 300 c.c. of hydrochloric acid (s. g. 1·19) cooled at 0°, so that the temperature does not rise above 10°, quickly filtering from sodium chloride, shaking the colourless filtrate in a separating funnel with 120 c.c. of toluene till sulphur begins to separate, running off the aqueous layer, and filtering the yellow toluene solution through a dry filter, when on standing at room temperature S_ϕ separates. At −80° an amorphous form separates from the solution. S_ϕ forms orange-yellow crystals and yellow solutions, not so strongly coloured as those of S_π (see below). It has a distinctive form and solubility, and the molecular weight in solution corresponds with S_6 (Beckmann, 1912).

Two other forms, S_ζ (rhombic plates) and S_η (hexagonal plates), nearly colourless, are formed by crystallising from a solution of sulphur in chloroform containing rubber and a little benzonitrile (Korinth, 1928).

Amorphous sulphur.—The changes which occur when sulphur is slowly heated to its boiling point are most remarkable.

EXPT. 3.—Small pieces of Sicilian roll sulphur slowly and carefully heated in a test-tube melt to a clear mobile yellow liquid, which does not wet the glass. On pouring in water S_β is produced. If the temperature is *gradually* raised and the tube shaken, the orange-red mobile liquid *suddenly* becomes very viscous at 180°–190°. At 230° the liquid is black and viscous. Beyond 230° the viscosity

decreases but the colour remains dark, and the sulphur boils at 444°. If the boiling sulphur is allowed to cool *slowly*, it passes through the above series of changes of colour and viscosity in the reverse order, solidifying as **β-sulphur.** But if the boiling liquid is *quickly* cooled by pouring into cold water it forms soft elastic transparent yellow threads, called **plastic sulphur** or **γ-sulphur.**

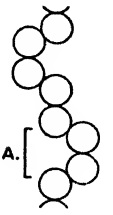


FIG. 293.—Structure of plastic sulphur.

Plastic sulphur (mentioned by Baumé in 1773) is amorphous but (like rubber) it shows an X-ray "fibre" diagram when stretched, suggesting that it contains long chains of sulphur atoms parallel to the direction of stretching (Fig. 293) (Trillat, 1932; Das, 1938). It is insoluble in carbon disulphide. On standing (more rapidly if stretched or heated at 100°) it forms an opaque brittle solid containing some rhombic sulphur, but mostly consisting of an amorphous form called S_μ insoluble in carbon disulphide. The soluble form has been called S_λ.

Plastic sulphur is obtained only from slightly impure sulphur which has been exposed to air and contains sulphuric acid. If ammonia gas is passed through the boiling sulphur, no plastic sulphur is formed on rapid cooling. In liquid sulphur S_λ and S_μ are in equilibrium at various temperatures: $S_\lambda \rightleftharpoons S_\mu$, and the percentages of S_μ are: at 120° 3·6, 160° 11, 444·6° over 30 (A. Smith, 1905–11; summary in Kruyt, *Z. phys. Chem.*, 1908, **64**, 513).

The rate of conversion of S_μ into S_λ on cooling is greatly increased by ammonia, which acts as a positive catalyst. Sulphur dioxide, sulphuric acid and traces of iodine act as negative catalysts, promoting the formation of S_μ on cooling, since they stabilise this form.

When pure sulphur is heated at 180° with 2 p.c. of sulphur chloride it remains mobile and supercooled when rapidly chilled, but becomes insoluble on solidification (Hammick, etc., *J.C.S.*, 1926, 1995; 1928, 797, 1785; 1930, 273). It has been supposed that the increase in viscosity of liquid sulphur at 180° is due to the meshing of chains of sulphur atoms formed by the rupture of S_8 rings (Warren, 1935); these chains may increase in length to 36 atoms at 250° and they persist on rapid cooling, when plastic sulphur is formed, but on slow cooling they re-form S_8 rings (Ewell and Eyring, *J. Chem. Phys.*, 1937, **5**, 726). It should not be overlooked, however, that many other properties of liquid sulphur besides the viscosity undergo rather *abrupt* changes at the thickening point (about 180°).

An amorphous variety called *white sulphur* remains as a pale yellow powder on extracting genuine flowers of sulphur with carbon disulphide, and is also precipitated when a solution of sulphur in carbon disulphide is exposed to light or by the action of water on sulphur chloride (p. 698). It is insoluble in carbon disulphide but forms a deep red solution in piperidine.

The form called S_π (apparently first noticed as "crumbly sulphur" by Magnus in 1856) is formed when the viscous sulphur at 180° is rapidly cooled. The solution in carbon disulphide deposits S_α at −80° and the solution on careful evaporation in vacuum at −80° deposits S_π. It forms a deep yellow solution in carbon disulphide (Aten, *Z. phys. Chem.*, 1913, **81**, 257; **83**, 442; 1914, **86**, 1; **88**, 321). Fused sulphur contains S_π, which depresses the freezing

point (S_μ does not) from 119·25° to 114·5° after some hours, from which it is calculated that 2·78 p.c. of S_π, with the molecular formula S_4, is present (Beckmann, 1918).

A white amorphous powder called *milk of sulphur*, soluble in carbon disulphide, is precipitated on acidifying a polysulphide solution (cf. p. 696).

EXPT. 4.—Boil 2 pts. of powdered sulphur with 13 of water and 1 pt. of lime slaked with 3 of water and filter the clear deep reddish-yellow liquid :

$$12S + 3Ca(OH)_2 = 2CaS_5 + CaS_2O_3 + 3H_2O.$$

This liquid was called *thion hudor* (*θεῖον ὕδωρ*, the " divine " or " sulphurous " water—Greek *theion* = sulphur) by Zosimos (A.D. 250). On adding hydrochloric acid it deposits a white precipitate of milk of sulphur (*lac sulphuris*) and evolves hydrogen sulphide—Zosimos says it is well to " hold the nose " :

$$2CaS_5 + CaS_2O_3 + 6HCl = 3CaCl_2 + 12S + 3H_2O.$$

Colloidal sulphur or S_θ is formed in the preparation of milk of sulphur and the filtered liquid is a turbid emulsion of sulphur. Sodium thiosulphate solution when acidified quickly forms a turbid colloidal suspension of sulphur. The milky liquid obtained when hydrogen sulphide is passed into sulphur dioxide solution deposits gum-like sulphur on evaporation, partly soluble in water (Debus, *J.C.S.*, 1888, **53**, 278).

Colloidal sulphur is obtained (Odén, 1913) by mixing 30 c.c. of 3*N* $Na_2S_2O_3$ solution and 10 c.c. of concentrated sulphuric acid, precipitating from solution by adding sodium chloride and centrifuging. It redissolves in water.

Some forms of colloidal sulphur are soluble and others insoluble in carbon disulphide. It is supposed that the insoluble form S_μ is first precipitated but may pass into the soluble form S_λ, this change being retarded by acidity, the presence of halogens, etc.

Sulphur vapour.—Sulphur boils at 444·60° and forms a deep red vapour, which when strongly heated becomes yellow. Dumas (1832) found the vapour density at 524° to correspond with S_6 ; it falls at higher temperatures, and at 1000° Bineau and Deville and Troost (1860) found it to correspond with S_2. Biltz (1888), over a wider range of temperature, found the densities (H = 1) : 468° 113 (higher than S_7), 524° 102 (higher than Dumas' figure), 606° 67. He concluded that S_6 does not form a definite constituent of the vapour. Bleier and Kohn (1900) lowered the boiling point to 193° at 2 mm. pressure, found a density corresponding with 7·85 atoms, and hence concluded that the molecule is S_8 ; this corresponds with the value found from the lowering of vapour pressure of carbon disulphide by rhombic sulphur. Preuner and Schupp (1910) consider that S_8, S_6 and S_2 can exist in the vapour. The density falls steeply between 500° and 850°, when it corresponds with S_2. Nernst (1903) found that 45 p.c. of the S_2 molecules are dissociated at 1900°–2000° : $S_2 \rightleftharpoons 2S$.

Vapour densities at 80° under low pressures (Neumann, *Z. phys. Chem.*, 1934, **171**, 416) give S_8 for S_α and S_β, and a smaller value (probably S_4) for S_μ.

Hydrogen Sulphides

Sulphur forms gaseous **hydrogen sulphide** H_2S, carefully investigated by Scheele (1777) who called it *fetid sulphurous air* and showed that it is a compound of hydrogen and sulphur, and liquid **hydrogen persulphides** H_2S_2, H_2S_3, H_2S_5 (and possibly H_2S_6), also obtained in a crude form by Scheele (1777).

H_2S : colourless gas, normal density 1·5392 g./lit., forming a colourless liquid, b.p. −60·7° and solid m.p. −85·6°; critical temperature 100·4°, critical pressure 89·05 atm.
H_2S_2 : pale yellow liquid, s. g. 1·496, m.p. −52·5°, b.p. 43°–50°/4·5 mm.
H_2S_3 : yellow liquid, s. g. 1·327, b.p. 74°–75°.
H_2S_5 : yellow oil.

Hydrogen sulphide.—When hydrogen is passed over boiling sulphur in a bulb-tube, the issuing gas contains 1 or 2 p.c. of hydrogen sulphide and blackens lead acetate paper. If pure hydrogen sulphide is heated, partial decomposition occurs, and the reaction is reversible : $H_2 + S \rightleftharpoons H_2S$. The equilibrium constants $K = [H_2][S_2]^{\frac{1}{2}}/[H_2S]$ are (Preuner and Schupp, 1907–9) :

°C.	-	750	830	945	1065	1132
$K \times 10^6$	-	1·06	4·2	24·5	107·5	226

The pure gas is best prepared synthetically in presence of pumice as a catalyst at 600°, when the reaction is practically complete (Corenwinder, 1852; Klemenc, *Z. anorg. Chem.*, 1932, **208**, 348). If powerful electric sparks pass through H_2S, sulphur is deposited and hydrogen remains. The gas is also decomposed by a heated platinum wire and by the silent discharge. The gas is evolved in a regular stream on heating a mixture of powdered sulphur, paraffin wax, and ignited asbestos.

Hydrogen sulphide is usually prepared by the action of dilute sulphuric acid (1 : 6) or better hydrochloric acid (1 : 3) on ferrous sulphide in a Kipp's apparatus : $FeS + 2HCl = FeCl_2 + H_2S$, and washing with a little water, but this gas contains a little hydrogen (from iron in the FeS). A gas free from hydrogen is obtained by heating powdered antimony sulphide (*stibnite*) with concentrated hydrochloric acid : $Sb_2S_3 + 6HCl = 2SbCl_3 + 3H_2S$. A pure gas is obtained from calcium sulphide and hydrochloric acid : $CaS + 2HCl = CaCl_2 + H_2S$ (Partington and Carroll, *Phil. Mag.*, 1925, **49**, 665); or by heating to 60° a solution of magnesium hydrosulphide obtained by passing the impure gas through magnesia suspended in water : $MgO + 2H_2S \rightleftharpoons Mg(HS)_2 + H_2O$.

Hydrogen sulphide may be collected by downward displacement; it attacks mercury slowly unless dry and free from oxygen. It can be dried for ordinary purposes with calcium chloride but it reacts with concentrated sulphuric acid : $H_2S + H_2SO_4 = S + SO_2 + 2H_2O$, and with unpurified P_2O_5. Dehydrated alumina can be used, but the best method of drying is liquefaction or solidification and distillation (Moissan, 1903; Linekin and Wilkinson, *J.A.C.S.*, 1940, **62**, 251).

Hydrogen sulphide is a colourless gas with a powerful smell of rotten eggs (decaying albumin evolves it) and is poisonous. It is somewhat heavier (1·2) than air. It liquefies by strong cooling or pressure (15 atm. at 12°) to a colourless liquid, which is a moderate solvent, especially for organic substances, but has little ionising power (Quam, *J.A.C.S.*, 1925, **47**, 103). The liquid has no action on potassium. At lower temperatures it freezes to a transparent solid.

The *formula* of hydrogen sulphide may be found by heating tin or copper in the gas (sodium cannot be used, as it forms NaHS). An equal volume of hydrogen remains, showing that the molecule is H_2S_x, and the density gives the molecular weight 34, hence $x = 1$ and the formula is H_2S. The two H—S bonds are practically at right angles (p. 268).

Hydrogen sulphide is moderately soluble in water (4·37 vols. at 0°, 3·40 vols. at 10°, 2·6 vols. at 20°), all the gas being evolved on boiling, and more soluble in alcohol (9·54 vols. at 15°). The solubility in water follows Henry's law. The solution in water is a weak acid and slowly evolves hydrogen with reduced iron. In decinormal solution it is 0·1 p.c. ionised to $H^{\cdot} + HS'$; the second stage of ionisation is very slight (Smith, *J.A.C.S.*, 1922, **44**, 1500):

$$[H^{\cdot}][HS']/[H_2S] = 9{\cdot}1 \times 10^{-8}, \quad [H^{\cdot}][S'']/[HS'] = 1{\cdot}2 \times 10^{-15}.$$

A crystal hydrate $H_2S,6H_2O$ is formed at low temperatures. The solution oxidises in presence of air and deposits sulphur: $2H_2S + O_2 = 2H_2O + 2S$, but this is retarded by adding $\frac{1}{50}$ the volume of glycerol.

Hydrogen sulphide is a reducing agent and the following reactions occur in solution:

$$H_2S + Cl_2 = 2HCl + S$$
$$H_2S + I_2 = 2HI + S$$
$$H_2S + H_2O_2 = 2H_2O + S$$
$$H_2S + 2FeCl_3 = 2FeCl_2 + 2HCl + S$$
$$22H_2S + 10KMnO_4 = 3K_2SO_4 + 2K_2S_2O_3 + 10MnS + 5S + 22H_2O$$
$$3H_2S + K_2Cr_2O_7 + 4H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + 3S + 7H_2O.$$

With a large excess of chlorine water sulphuric acid is formed:

$$S + 4H_2O + 3Cl_2 = H_2SO_4 + 6HCl.$$

The gas ignites in air at 364° and burns in air or oxygen with a blue flame; it is completely dissociated in the flame, which deposits sulphur on a cold porcelain dish. If the gas in a glass cylinder is kindled at the mouth, a deposit of sulphur forms inside the jar: $2H_2S + O_2 = 2S + 2H_2O$. With a plentiful supply of oxygen, sulphur dioxide is formed: $2H_2S + 3O_2 = 2SO_2 + 2H_2O$. A mixture of 2 vols. of hydrogen sulphide and 3 vols. of oxygen explodes violently when kindled.

Hydrogen sulphide gas or solution (*e.g.* sulphur waters) blackens lead acetate paper, lead sulphide being formed. Alkali sulphides (but not free hydrogen sulphide) give a purple colour with freshly prepared sodium nitroprusside solution (p. 863).

Fuming nitric acid reacts violently with hydrogen sulphide gas, ignition and perhaps explosion occurring, and a jet of the gas ignites in euchlorine (a mixture of chlorine and ClO_2, p. 794).

Dilute (5. p.c.) nitric acid does not react; more concentrated (43 p.c.) gives sulphur, sulphuric acid, ammonia, nitrous oxide, nitric oxide and nitrous acid. A solution containing 15 p.c. of sulphuric acid and 23 p.c. of nitric acid, whether mixed or formed by the reaction itself, is inert towards the gas (Dunnicliff and Mohammad, *J. Phys. Chem.*, 1929, **33**, 1343).

Hydrogen sulphide is a weak acid and is absorbed by alkali hydroxide solutions, forming *sulphides*, and with excess of hydrogen sulphide these form *hydrosulphides*:

$$H_2S + 2NaOH = Na_2S + 2H_2O$$
$$H_2S + Na_2S = 2NaHS.$$

These are hydrolysed and the solutions are alkaline:

$$S'' + H_2O \rightleftharpoons HS' + OH'; \quad HS' + H_2O \rightleftharpoons H_2S + OH'.$$

The precipitation of metal sulphides in acid (Group II) and alkaline (Group IV) solutions is used in qualitative analysis and depends on the different solubility products (p. 168). Since the concentration of S'' ions is very small, especially in acid solutions, hydrosulphides may be the first products (Middleton and Ward, *J.C.S.*, 1935, 1459).

Hydrogen persulphides.—When the yellow solution (*thion hudor*) of polysulphides of calcium (p. 693) is poured in a thin stream into cold fairly concentrated hydrochloric acid, with constant stirring, a yellow oil (noticed by Scheele, 1777) separates, which Thenard (1831) regarded as *hydrogen persulphide* H_2S_2, analogous to hydrogen peroxide H_2O_2:

$$CaS_2 + 2HCl = CaCl_2 + H_2S_2.$$

EXPT 5.—To 250 c.c. of a cooled mixture of equal volumes of concentrated HCl and water in a beaker add in a thin stream, with vigorous stirring, 100 c.c. of *thion hudor*. Litmus paper in the milky liquid is bleached. Pour the liquid into a separating funnel. After a few hours a yellow oil, heavier than water (s. g. 1·7) separates.

The oil has a pungent smell and is soluble in benzene and carbon disulphide, but sparingly soluble in and decomposed by alcohol. It slowly decomposes spontaneously, especially on warming, into hydrogen sulphide and sulphur. The composition is variable, since sulphur formed by its decomposition dissolves in the persulphide. Rebs (1888) considered it to be H_2S_5, but it is probably a solution of sulphur in H_2S_2 and H_2S_3:

$$2CaS_5 + 4HCl = 2CaCl_2 + H_2S_2 + H_2S_3 + 5S.$$

Sabatier (1885) separated the crude persulphide into fractions by distillation at 40–100 mm. pressure; the chief fraction was intermediate between H_2S_2 and H_2S_3, and he thought it was H_2S_2 and dissolved sulphur. Bloch and Höhn (*Ber.*, 1908, **41**, 1961; Butler and Maas, *J.A.C.S.*, 1930, **52**, 2184) used glass

vessels washed with hydrochloric acid to remove alkali, which decomposes the persulphide, separated the crude oil and dried it with calcium sulphide which had been treated with hydrogen chloride gas. They distilled the oil in small lots at a time at 2 mm. pressure, the residue in the distillation flask being removed before a new portion of oil was distilled (Fig. 294). The distillate was collected in two receivers. In the first receiver **hydrogen trisulphide** H_2S_3, a pale yellow liquid, s. g. 1·496, b.p. 43°–50°/4·5 mm., m.p. −52° to −53°, collected. In the second, more strongly cooled receiver, **hydrogen disulphide** H_2S_2, a yellow liquid, colourless at low temperature, s. g. 1·327, b.p. 74°–75°, collected; it is quickly decomposed by water and alkalis.

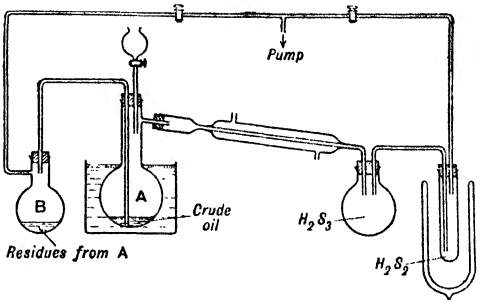


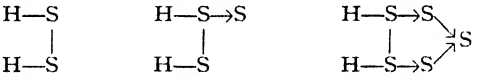
FIG. 294.—Preparation of hydrogen persulphides.

Hydrogen pentasulphide H_2S_5 is formed (Mills and Robinson, *J.C.S.*, 1928, 2326) as a clear yellow oil (which decomposes on distillation) by the reaction between ammonium pentasulphide crystals and anhydrous formic acid:

$$(NH_4)_2S_5 + 2H{\cdot}COOH = 2H{\cdot}COONH_4 + H_2S_5.$$

The ammonium pentasulphide separates in yellow crystals from the deep red solution formed by passing hydrogen sulphide, in absence of air, into 40 g. of powdered sulphur suspended in 100 c.c. of ammonia solution (s. g. 0·88).

The formulae of the hydrogen persulphides may be:



The solubility curves of sulphur in H_2S_2 and in H_2S_3 between −34·72° and 55·3° are identical and show a marked break at −1·45°, when the liquid has very nearly the composition H_2S_6 (Walton and Whitford, *J.A.C.S.*, 1923, **45**, 601).

HALOGEN COMPOUNDS OF SULPHUR

S_2F_2 gas, m.p. −105·5°, b.p. −99°	S_2Cl_2 yellow liquid, m.p. −80°, b.p. 138°	S_2Br_2 red liquid, s. g. 2·635, m.p. −46°, b.p. 57°/0·22 mm.
SF_4 gas, m.p. −124°, b.p. −40°	S_3Cl_4, m.p. −103°	
S_2F_{10} liquid, m.p. −92°, b.p. 29°	SCl_2 red liquid	
SF_6 gas, m.p. −50·8°, b.p. −63·8°	SCl_4 yellowish-brown liquid, m.p. −30°	

All the fluorides are colourless. SF_6 melts under pressure at a higher temp. than its b.p. at 1 atm. The supposed iodides of sulphur are mixtures (Smith and Carson, *Z. phys. Chem.*, 1908, **61**, 200; Wright, *J.C.S.*, 1915, **107**, 1527).

Sulphur burns spontaneously in fluorine forming gaseous **sulphur hexafluoride** SF_6 (Moissan and Lebeau, 1900; Schumb and Gamble, *J.A.C.S.*, 1930, **52**, 4302). Sulphur hexafluoride has the normal density. It is insoluble in water and chemically very inert; even fused caustic potash and ignited copper oxide and lead chromate do not decompose it, but it reacts with hydrogen sulphide: $SF_6 + 3H_2S = 6HF + 4S$, and boiling sodium: $SF_6 + 8Na = Na_2S + 6NaF$.

The molecule SF_6 probably has a 12-electron shell with six covalent bonds, and (like SeF_6 and TeF_6) a regular octahedral structure (Brockway and Pauling, 1933).

Sulphur monofluoride S_2F_2, obtained by heating silver fluoride with sulphur: $2AgF + 3S = Ag_2S + S_2F_2$, and **sulphur tetrafluoride** SF_4, formed by heating cobaltic fluoride with sulphur: $4CoF_3 + S = 4CoF_2 + SF_4$, are unconfirmed. A small amount of **sulphur pentafluoride** S_2F_{10} is formed along with SF_6 by the action of fluorine on sulphur (Denbigh and R. Whytlaw-Gray, *J.C.S.*, 1934, 1346).

Sulphur monochloride S_2Cl_2 (Thomson, 1803) is made by passing dry chlorine over sulphur fused in a retort and distilling (b.p. 138°) into a dry receiver. The red liquid is purified by distilling over sulphur, or better by shaking with active charcoal, when the small excess of chlorine is removed and a clear amber-yellow liquid, s. g. 1·6733 at 25° is obtained (W. J. Pope, *J.C.S.*, 1921, **119**, 634; Harvey and Schuette, *J.A.C.S.*, 1926, **48**, 2065).

The vapour density agrees with the formula S_2Cl_2 but the liquid dissociates slightly on heating, becoming red. It fumes in moist air and has a very disagreeable pungent smell. The stoppers of bottles containing it become coated with sulphur, owing to hydrolysis. The liquid is only slowly hydrolysed by water, forming hydrochloric acid, sulphur, sulphur dioxide and oxyacids of sulphur. The primary reaction is probably:

$$S_2Cl_2 + 2H_2O = SO_2 + H_2S + 2HCl,$$

the sulphur dioxide and hydrogen sulphide then reacting, mainly as:

$$2H_2S + SO_2 = 3S + 2H_2O,$$

but also forming some pentathionic acid (Alin, *J.A.C.S.*, 1926, **48**, 167; see pentathionic acid). Metals decompose it on heating, forming sulphides and chlorides. Sulphur chloride dissolves sulphur (66 p.c.), iodine, many metal halides, and organic compounds. It forms a compound $S_2Cl_2,4HCl$ (Terrey and Spong, *J.C.S.*, 1932, 219). The liquid has a small dielectric constant (4·9) and weak ionising power. The structure is probably Cl·S·S·Cl (Ackermann and Mayer, *J. Chem. Phys.*, 1936, **4**, 377).

By saturating sulphur monochloride with chlorine at room temperature the ruby-red liquid **sulphur dichloride** SCl_2 is formed, but this decomposes into S_2Cl_2 and chlorine on distillation. At −22° chlorine and sulphur monochloride form **sulphur tetrachloride** SCl_4, a yellowish-brown liquid decomposing and giving off chlorine at a higher temperature. It freezes to a yellowish-white solid. It forms stable double chlorides, *e.g.* amber crystals of $SCl_4,SbCl_5$ (Partington, *J.C.S.*, 1929, 2573).

The sulphur-chlorine system is rather complicated (Lowry, etc., *J.C.S.*, 1927, 746; 1929, 1421; 1930, 1005; 1931, 323; 1934, 485, 1283). Chlorinated sulphur chloride after heating at 100° in a sealed tube gives freezing-point maxima (Fig. 295) corresponding with S_2Cl_2 and SCl_4, and breaks corresponding with the crystallisation of SCl_2 and S_3Cl_4. Although an equilibrium mixture of the composition SCl_2 deposits SCl_4 on freezing, freshly prepared mixtures of S_2Cl_2 with an over-chlorinated sample of SCl_2 give a temporary freezing-point maximum corresponding with SCl_3, and solid SCl_2 can be frozen out of the fresh mixture and crystallised from light petroleum by cooling in liquid air.

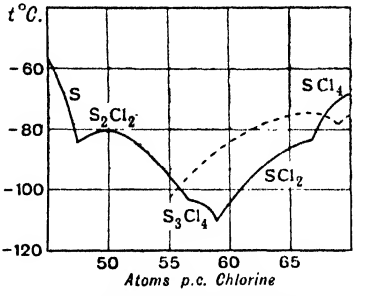


FIG. 295.—The sulphur-chlorine system.

Sulphur monobromide S_2Br_2 is a garnet-red liquid formed by heating the elements in a sealed tube.

OXYGEN COMPOUNDS OF SULPHUR

The following oxides and oxyacids (or their salts) of sulphur are known:

Oxides:

SO gas.
SO_2 gas, m.p. −75·5°, b.p. −10·0°, crit. temp. 157·15°, crit. press. 75·65 atm.
S_2O_3 green solid.
SO_3 solid, 3 forms, m.ps. 16·8°, 32·5°, 62·2°, b.p. 44·52°.
S_2O_7 or SO_4 or S_3O_{11}, solid, m.p. *c.* 0°.

Acids:

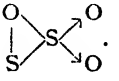
Sulphoxylic H_2SO_2 (known only as salts).
Hyposulphurous (*dithionous*) $H_2S_2O_4$ (known only as salts).
Sulphurous H_2SO_3 and **disulphurous** $H_2S_2O_5$ (known only as salts).
Sulphuric H_2SO_4, liq., m.p. 10·49°, b.p. 338°, and **disulphuric** $H_2S_2O_7$, liq., m.p. 35°.
Thiosulphuric $H_2S_2O_3$ (known only as salts).
Permonosulphuric H_2SO_5, solid, m.p. 45° (decomp:).
Perdisulphuric $H_2S_2O_8$, solid, m.p. 65° (decomp.).
Thionic acids $H_2S_nO_6$ (known in solution and as salts): *dithionic* $H_2S_2O_6$, *trithionic* $H_2S_3O_6$, *tetrathionic* $H_2S_4O_6$, *pentathionic* $H_2S_5O_6$, and *hexathionic* $H_2S_6O_6$.

Sulphur monoxide SO (Cordes and Schenck, 1933) is formed by (i) the slow oxidation of sulphur on heating in air, (ii) burning sulphur in oxygen below 40 mm. pressure, (iii) the action of an electric discharge on a mixture of sulphur dioxide and sulphur vapour at 10 mm. pressure: $S + SO_2 = 2SO$, and (iv) the action of finely divided silver on thionyl chloride: $SOCl_2 + 2Ag = SO + 2AgCl$.

It is a colourless gas stable at room temperature but decomposed at 100°: $2SO = SO_2 + S$. It combines with oxygen only on sparking, readily combines with chlorine and bromine at 0·3 mm. pressure to form $SOCl_2$ and $SOBr_2$, and is

absorbed by alkali forming sulphide, sulphite and thiosulphate. On cooling the gas an orange-red condensate is formed which does not form SO on warming. The molecule may be S=O or S→O.

Sulphur sesquioxide (F. C. Vogel, 1812; Weber, 1875; Vogel and Partington, *J.C.S.*, 1925, **127**, 1514; Wöhler and Wegwitz, 1933) is a malachite-green solid formed by the action of liquid sulphur trioxide on powdered sulphur: $S + SO_3 = S_2O_3$. It is very unstable, decomposing at room temperature and rapidly on warming: $2S_2O_3 = S + 3SO_2$; some SO may be formed: $S_2O_3 = SO + SO_2$. It dissolves in concentrated sulphuric acid to an indigo-blue liquid, but is violently decomposed by water, forming sulphur, sulphuric acid, trithionic acid, and smaller amounts of sulphurous and pentathionic acids. The molecule may be



Sulphur Dioxide

Sulphur dioxide was discovered by Priestley in 1774 by heating mercury with concentrated sulphuric acid and collecting the gas (*vitriolic acid air*) over mercury: $Hg + 2H_2SO_4 = HgSO_4 + SO_2 + 2H_2O$. A similar reaction occurs with copper: $Cu + 2H_2SO_4 = CuSO_4 + SO_2 + 2H_2O$, and silver: $2Ag + 2H_2SO_4 = Ag_2SO_4 + SO_2 + 2H_2O$.

Expt. 6.—Copper turnings are covered with three times their weight of concentrated sulphuric acid in a flask fitted with a thistle funnel, and heated on wire gauze. The mixture becomes dark and gas is evolved with effervescence. When this occurs the flame is lowered or removed. The gas is collected by downward displacement (it is 2¼ times as heavy as air) or over mercury. It may be dried by concentrated sulphuric acid, calcium chloride, or phosphorus pentoxide.

Concentrated sulphuric acid is also reduced on heating with charcoal: $C + 2H_2SO_4 = CO_2 + 2SO_2 + 2H_2O$, and (very slowly) when boiled with sulphur: $S + 2H_2SO_4 = 3SO_2 + 2H_2O$, and sulphur dioxide is formed by the combustion of sulphur in oxygen or air: $S + O_2 = SO_2$, and is made on the large scale (mixed with nitrogen) by roasting iron pyrites (or other sulphide minerals) in air: $4FeS_2 + 11O_2 = 2Fe_2O_3 + 8SO_2$.

Melted sulphur phosphoresces feebly in air at 230°, forming SO_2 and some SO (Heumann, 1883). It inflames at about 363° in air and 275°–280° in oxygen (unless the materials are very dry: see p. 483), burning with a blue flame to sulphur dioxide and a little trioxide (which makes the gas cloudy). The volume is unchanged, $xS + O_2 = S_xO_2$, hence the formula is S_xO_2 and the density of sulphur dioxide shows that $x = 1$, hence the formula is SO_2.

Expt. 7.—Heat a small piece of sulphur in a metal spoon, by means of an electrically heated fine platinum wire, in dry oxygen over mercury in the apparatus shown in Fig. 224. On cooling the volume of gas is unchanged.

Sulphur dioxide is evolved by the action of acids on sulphites, *e.g.* by dropping concentrated sulphuric acid into concentrated sodium hydrogen sulphite solution: $NaHSO_3 + H_2SO_4 = NaHSO_4 + SO_2 + H_2O$.

Sulphur dioxide is a colourless gas with a choking smell, normal density 2·9267 g. per lit., easily liquefied by compression (2·5 atm. at 15°) or passing through a spiral cooled in a freezing mixture of ice and salt (Fig. 250) to a colourless liquid, density 1·434 at 0°, which on rapid evaporation forms a snow-like solid. The liquid is made technically; it dissolves iodine, sulphur, phosphorus, resins and some salts and can be used as a reaction solvent (Ross, etc., *Ind. Eng. Chem.*, 1942, **34**, 924), and has some ionising power (dielectric constant 13·75). It can be kept in iron vessels, and is used as a source of the gas and in purifying petroleum by washing (Johnstone, *Ind. Eng. Chem.*, 1942, **34**, 1017).

Sulphur dioxide is very stable and is not decomposed by heat. On exposure to light it decomposes into sulphur and sulphur trioxide, becoming cloudy (Morren, 1870; Berthelot and Gaudechon, 1910; Hill, *Trans. Faraday Soc.*, 1924, **20**, 107): $3SO_2 = 2SO_3 + S$.

Sulphur dioxide extinguishes a burning taper but heated potassium burns in it, forming sulphite and thiosulphate: $4K + 3SO_2 = K_2SO_3 + K_2S_2O_3$, and finely divided iron and tin burn to form oxides and sulphides. It reacts with strongly heated carbon (p. 689), copper: $3Cu + 2SO_2 = Cu_2S + CuSO_4$, copper oxide: $3CuO + SO_2 = Cu_2O + CuSO_4$, and other metal oxides (Hammick, *J.C.S.*, 1917, **111**, 379). When passed over brown lead dioxide warmed in a bulb tube white lead sulphate is formed with incandescence: $PbO_2 + SO_2 = PbSO_4$.

Sulphur dioxide is freely soluble in water, 45 vols. to 1 of water at 15°, forming a liquid smelling strongly of the gas and acid to litmus.

The solubilities in g. per 100 g. H_2O when $p_{SO_2} = 760$ mm. are (Hudson, *J.C.S.*, 1925, **127**, 1332):

10°	15°	20°	25°	30°	50°
15·4	12·6	10·5	8·96	7·7	4·2

One vol. of glacial acetic acid absorbs 318 vols. or nearly its own weight of sulphur dioxide at 15°. The aqueous solution probably contains sulphurous acid H_2SO_3, but this cannot be isolated. The ionisation constants at 25° are (Tartar and Garretson, *J.A.C.S.*, 1941, **63**, 808):

$$K_1 = [H^+][HSO_3^-]/[H_2SO_3] = 1{\cdot}72 \times 10^{-2}$$
$$K_2 = [H^+][SO_3^{--}]/[HSO_3^-] = 6{\cdot}24 \times 10^{-8}.$$

On boiling, all the sulphur dioxide is evolved. On strongly cooling the saturated solution crystals of the hydrate $SO_2,6H_2O$ separate (Tammann and Krige, 1925). The solution when heated in a sealed tube at 150° deposits sulphur: $3H_2SO_3 = 2H_2SO_4 + H_2O + S$. The solution has weak bleaching properties; moist wool, straw and other materials injured by chlorine are bleached by exposure to sulphur dioxide or the fumes of burning sulphur. This has been explained by: (i) the formation of colourless addition compounds with the colouring matters, or (ii) the reduction of the colours to colourless compounds, possibly by nascent hydrogen: $SO_2 + 2H_2O = H_2SO_4 + 2H$.

Sulphurous acid (and sulphite) solutions are oxidised by atmospheric oxygen to sulphuric acid (and sulphates), the reaction being strongly catalysed by traces

of copper or iron salts (p. 143) but retarded by glycerol, mannitol, phenol, benzaldehyde and (especially) stannous chloride. A chain reaction is supposed to occur, involving the ion SO_3' which behaves as a free radical (Franck and Haber, 1931).

Sulphurous acid evolves hydrogen with magnesium powder and is reduced to hydrogen sulphide by nascent hydrogen (zinc and dilute hydrochloric acid). It is a *reducing agent*. It precipitates mercury from mercurous nitrate solution: $Hg_2(NO_3)_2 + SO_2 + 2H_2O = 2Hg + 2HNO_3 + H_2SO_4$, but mercuric chloride is reduced to mercurous chloride and some mercury only on boiling. Iodine is liberated from an iodate (p. 806):

$$2IO_3' + 5HSO_3' + 2H^{\cdot} = I_2 + 5HSO_4' + H_2O,$$

but with excess of sulphur dioxide the iodine is decolorised:

$$I_2 + SO_2 + 2H_2O = 2HI + H_2SO_4.$$

Permanganate solution is decolorised:

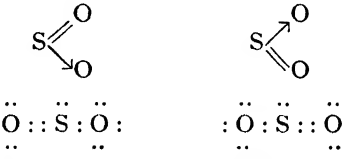
$$2KMnO_4 + 5SO_2 + 2H_2O = K_2SO_4 + 2MnSO_4 + 2H_2SO_4$$

and orange-yellow acidified dichromate solution is turned green:

$$2CrO_3 + 3SO_2 = Cr_2(SO_4)_3.$$

Sulphur dioxide in presence of concentrated hydrochloric acid can sometimes act as an oxidising agent, sulphur being deposited: ferrous, cuprous and stannous chlorides form ferric, cupric and stannic salts (Wardlaw, etc., *J.C.S.*, 1920–23): $SO_2 + 4H^{\cdot} = 2H_2O + S + 4\oplus$; $4Fe^{\cdot\cdot} + 4\oplus = 4Fe^{\cdot\cdot\cdot}$, etc.

The SO_2 molecule cannot have two double bonds O=S=O as this molecule would be linear and have no dipole moment, whereas SO_2 has a moment of 1·6 D. The molecule is bent and there is probably resonance between the forms



(Schomacher and Stevenson, *J.A.C.S.*, 1940, **62**, 1270; Pauling, *The Nature of the Chemical Bond*, 1940, 247). The S to O distance is 1·43 A., slightly less than in the SO_4'' ion, and the O—S—O angle 121°. The SeO_2 molecule has a similar structure (Palmer and Elliott, *J.A.C.S.*, 1938, **60**, 1309) with Se to O 1·61 A., approximately the same as for the SeO_4'' ion.

Sulphites.—Sulphurous acid is dibasic and forms two series of salts, the *acid sulphites* which should theoretically have the formula M^IHSO_3, and the *normal sulphites* $M_2^ISO_3$.

EXPT. 8.—Divide a solution of caustic soda into two equal parts. Saturate one with SO_2, producing a solution of sodium hydrogen sulphite $NaHSO_3$. This is acid, owing to the reaction: $2HSO_3' = S_2O_5'' + H_2O \rightleftharpoons 2SO_3'' + 2H^{\cdot}$. Mix this

with the other half of the caustic soda and evaporate. Crystals of normal sodium sulphite $Na_2SO_3,7H_2O$ are produced on cooling.

Normal alkali sulphites give slightly alkaline solutions, owing to hydrolysis : $SO_3'' + H_2O \rightleftharpoons HSO_3' + OH'$. Phenolphthalein is not reddened by a *concentrated* solution of sodium sulphite unless heated, and the colour disappears on cooling (Raschig). Barium chloride gives a white precipitate of barium sulphite $BaSO_3$, soluble in hydrochloric acid (cf. $BaSO_4$) : chlorine or bromine water precipitates barium sulphate from the solution :

$$SO_3'' + H_2O + Cl_2 = SO_4'' + 2Cl' + 2H'.$$

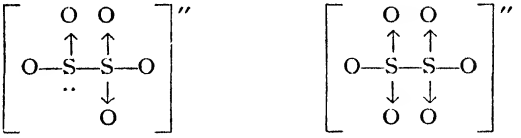
Sulphites are $Na_2SO_3,7H_2O$, K_2SO_3, Ag_2SO_3 (white pp.), $CaSO_3$ (sparingly soluble), $MgSO_3,3H_2O$, $ZnSO_3,2\frac{1}{2}H_2O$, $Al_2(OH)_4SO_3$, Tl_2SO_3, $PbSO_3$ (white pp.), $MnSO_3,3H_2O$, $FeSO_3,2\frac{1}{2}H_2O$, and many double and complex salts.

The *acid sulphites* are unstable, but solid $KHSO_3$ (monoclinic with different axial ratios and angle from those of $K_2S_2O_5$) is described. The solutions generally have a distinct greenish colour.

By evaporating a solution saturated with sulphur dioxide, or passing sulphur dioxide over crystals of Na_2CO_3,H_2O, solid **sodium disulphite** (or *pyrosulphite*) $Na_2S_2O_5$ is formed. The potassium salt $K_2S_2O_5$ crystallises from a hot saturated solution of potassium carbonate saturated with sulphur dioxide. These salts are sometimes called *metabisulphites* ($Na_2O,2SO_2$).

On heating, disulphites decompose : $Na_2S_2O_5 = Na_2SO_3 + SO_2$, and normal sulphites form sulphate and sulphide : $4Na_2SO_3 = 3Na_2SO_4 + Na_2S$.

The Raman spectrum indicates that even in solution the ion of acid sulphites is S_2O_5'' and not HSO_3' (Fadda, 1932). The disulphite ion has the structure $O_2S—SO_3$ and not $O_2S—O—SO_2$ (Zachariasen, *Phys. Rev.*, 1932, **40**, 923) and is similar to the dithionate ion except that an unshared pair of electrons takes the place of an oxygen atom :



The S to O distance is 1·46 Å., the S to S 2·18 Å.

Thionyl Halides

Thionyl fluoride SOF_2, colourless gas, m.p. − 110°, b.p. − 30°.
Thionyl chloride $SOCl_2$, colourless liquid, d. 1·677/0°, m.p. − 104·5°, b.p. 78°.
Thionyl bromide $SOBr_2$, red liquid, m.p. − 52°, b.p. 59°/40 mm.

These compounds contain the bivalent thionyl radical =SO, and may be regarded as halides of the hypothetical sulphurous acid $SO(OH)_2$.

Thionyl fluoride SOF_2 is a colourless fuming gas, stable at high temperature, formed by heating arsenic trifluoride and thionyl chloride in a sealed tube at

100° : $2AsF_3 + 3SOCl_2 = 3SOF_2 + 2AsCl_3$ (Moissan and Lebeau, 1900) ; or heating nitrogen sulphide with liquid slightly moist hydrogen fluoride in presence of a little copper oxide at 100° (Ruff and Thiel, 1905).

It is slowly hydrolysed by water : $SOF_2 + H_2O = SO_2 + 2HF$, and slowly absorbed by heated sodium. With dry ammonia it forms $2SOF_2,5NH_3$ and $2SOF_2,7NH_3$.

Thionyl chloride $SOCl_2$ is formed by the action of sulphur dioxide on phosphorus pentachloride

$$SO_2 + PCl_5 = \underset{\text{b.p. } 78°}{SOCl_2} + \underset{\text{b.p. } 107°}{POCl_3}$$

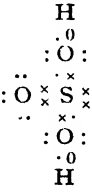
and fractionating the liquid product. It is also formed by the addition of sulphur to chlorine monoxide at −12° : $Cl_2O + S = SOCl_2$, and is manufactured by adding sulphur trioxide to sulphur chloride at 75°–80°, and passing a stream of chlorine through the mixture to reconvert the separated sulphur into the chloride : $SO_3 + S_2Cl_2 = SOCl_2 + SO_2 + S$.

Thionyl chloride is a colourless mobile liquid, fuming in moist air and decomposed by water : $SOCl_2 + H_2O = SO_2 + 2HCl$.

Thionyl bromide $SOBr_2$ is a red liquid formed by acting on $SOCl_2$ with gaseous HBr : $SOCl_2 + 2HBr = SOBr_2 + 2HCl$. The supposed thionyl chlorobromide SOClBr, said by Besson also to be formed in this reaction, is a mixture of $SOCl_2$ and $SOBr_2$ (Mayes and Partington, *J.C.S.*, 1926, 2594).

The constitution of sulphurous acid.—The formation of sulphurous acid by the action of water on thionyl chloride Cl·SO·Cl suggests that it has the symmetrical formula HO·SO·OH. By the action of thionyl chloride on alcohol symmetrical diethyl sulphite EtO·SO·OEt, b.p. 161°, is formed. By oxidising mercaptan EtSH with dilute nitric acid ethylsulphonic acid $EtSO_3H$ is formed, the ethyl ester of which, $EtSO_3Et$, is obtained by the action of sodium sulphite on ethyl iodide. In the sulphonic acid the ethyl group is directly attached to sulphur, as in mercaptan. Sulphurous acid, therefore, appears to possess two formulae, the *symmetrical* HO·SO·OH, and the *unsymmetrical* $H·SO_2·OH$ (sulphonic acid).

The symmetrical formula may be written :



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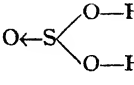
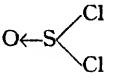
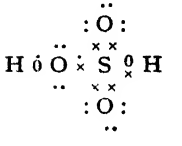


and thionyl chloride



The unsymmetrical formula and that for a sulphonic acid (R = Et, etc.) may be written :



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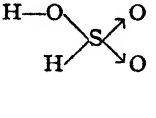

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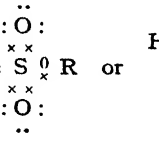

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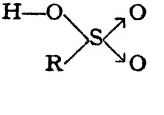
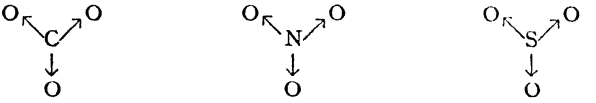


The bond distances in the compounds, however, show a considerable amount of double bond character, as in the formulae previously adopted :

and the actual state of sulphurous acid is probably a resonance hybrid (p. 270).

It has been usual to represent the carbonate, nitrate and sulphite ions, which show isomorphism, as symmetrical triangular structures :



but the isomorphism of sulphites and carbonates is imperfect (Langmuir *J.A.C.S.*, 1919, **41**, 1543), the bond distances all show a large amount of double bond character, and the CO_3'' and NO_3' ions are planar, but SO_3'' pyramidal.

Sulphur Trioxide

Sulphur trioxide is formed from sulphur dioxide and ozone : $3SO_2 + O_3 = 3SO_3$, but is usually prepared by passing a dry mixture of sulphur dioxide and oxygen over heated platinised asbestos, which acts as a catalyst :

$$2SO_2 + O_2 \rightleftharpoons 2SO_3.$$

Expt. 9.—Pass sulphur dioxide and oxygen through concentrated sulphuric acid and then over platinised asbestos heated in a hard glass tube (Fig. 296). The sulphur trioxide condenses to white crystals (sometimes a liquid separates first) in a test-tube cooled in a freezing mixture. The whole apparatus must be dry.

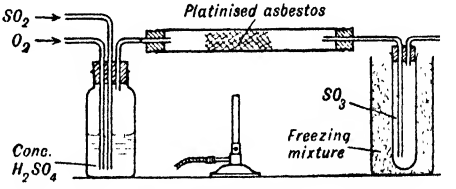


Fig. 296.—Preparation of sulphur trioxide.

Sulphur trioxide is formed by distilling concentrated sulphuric acid with a large excess of phosphorus pentoxide (SO_3 itself is a powerful dehydrating agent) : $H_2SO_4 + P_2O_5 = SO_3 + 2HPO_3$, and is conveniently made on a small scale by distilling fuming sulphuric acid in a retort and collecting the trioxide in a perfectly dry receiver cooled in a freezing mixture : $H_2S_2O_7 = H_2SO_4 + SO_3$. Sulphur trioxide is evolved on heating sodium disulphate, ferric sulphate, or dry ferrous sulphate to redness, but some of it is decomposed at the high temperature :

$$Na_2S_2O_7 = Na_2SO_4 + SO_3$$
$$Fe_2(SO_4)_3 \rightleftharpoons Fe_2O_3 + 3SO_3$$
$$2FeSO_4 = Fe_2O_3 + SO_3 + SO_2.$$

Sulphur trioxide exists in more than one modification. The liquid first obtained on cooling the vapour solidifies to transparent crystals, m.p. 16·8°, s. g. 1·9255 at 20°. This is called α-SO_3. On standing, at least in presence

of a trace of moisture, it forms silky asbestos-like crystals of β-SO_3, and there may be two forms of this, m.ps. 32·5° and 62·2° (Smits and Schoenmaker, *J.C.S.*, 1924, **125**, 2554; 1926, 1108, 1603). At 50°, the β-form changes slowly into the α-form.

The vapour density of sulphur trioxide corresponds with SO_3. Molecular weight determinations in $POCl_3$ (supposed to give S_2O_6 for the β-form) are vitiated by reactions with the solvent (Oddo, 1927). When passed through a red-hot tube the vapour decomposes to 2 vols. of SO_2 and 1 vol. of O_2, which do not recombine on cooling in absence of a catalyst: $2SO_3 = 2SO_2 + O_2$. The solid absorbs atmospheric moisture with avidity, giving dense white fumes of droplets of sulphuric acid: $H_2O + SO_3 = H_2SO_4$. It dissolves in water with a loud hissing noise and much heat, but dissolves quietly in concentrated sulphuric acid; the fuming acid so obtained solidifies on cooling to colourless crystals of **disulphuric acid** or **pyrosulphuric acid** $H_2S_2O_7$, m.p. 35°. Sulphur trioxide reacts violently with baryta, the mass becoming incandescent: $SO_3 + BaO = BaSO_4$. It combines with sodium chloride, the complex decomposing at 279°–350° (Salley, *J.A.C.S.*, 1939, **61**, 834): $2NaCl + 3SO_3 = Na_2S_2O_7 + SO_2 + Cl_2$.

Sulphuric Acid

The contact process.—Fuming sulphuric acid (*oleum*) is made technically from sulphur trioxide obtained by passing a purified mixture of sulphur dioxide and air over a heated catalyst, usually platinum or vanadium pentoxide. The reaction is strongly exothermic: $2SO_2 + O_2 \rightleftharpoons 2SO_3 + 45$ k. cal., and Le Chatelier's principle (p. 134) shows that the *equilibrium* yield of SO_3 decreases at higher temperatures. The reaction velocity is too slow below 400° even in presence of the catalyst, so that some temperature above this must be used (Lewis and Ries, *Ind. Eng. Chem.*, 1925, **17**, 593; 1927, **19**, 830). The reaction is reversible and from the law of mass action: $[SO_3]^2/[SO_2]^2[O_2] = K$, the yield is increased by excess of oxygen. A gas obtained by burning sulphur or iron pyrites in excess of air, containing by volume about 7 p.c. of SO_2, 10·5 p.c. of free oxygen and 82·5 p.c. of nitrogen is used, and with this the percentages of SO_2 oxidised to SO_3 in equilibrium are: 434° 99, 550° 85, 645° 60. The working temperature with a platinum catalyst is 400°–450°.

Values of K (Bodenstein and Pohl, *Z. Elektrochem.*, 1905, **11**, 371):

$t°$ C. -	528	627	727	832	897
K -	$6·44 \times 10^4$	$3·16 \times 10^3$	$2·83 \times 10^2$	$3·57 \times 10$	$1·23 \times 10$

agree with the equation ($T = t°$ C. + 273):

$$\log K = 10373/T + 2·222 \log T - 14·585.$$

The contact process was patented by Peregrine Phillips of Bristol in 1831 (Winteler, *Z. angew. Chem.*, 1905, **18**, 1512, 1654) and was used to make fuming sulphuric acid by Squire and Messel (*J.S.C.I.*, 1885, **4**, 520) from 1875, the gas being made by dropping concentrated sulphuric acid on red-hot bricks and drying with concentrated sulphuric acid: $2H_2SO_4 = 2SO_2 + O_2 + 2H_2O$.

The first attempts to use the gas from burnt pyrites failed, as the platinum catalyst was rapidly poisoned by impurities such as arsenic oxide and dust. About 1898 Knietsch (*Ber.*, 1901, **34**, 4069; bibl.) of the Badische Company, and Krauss and von Berneck, after much research, showed that the arsenious oxide, sulphuric acid fog, and dust in the gas from pyrites burners are removed by adding some steam and cooling, or washing with water, and then filtering the gas through coke wetted with concentrated sulphuric acid. The gas must be "optically clear," *i.e.* no fog is seen in a powerful beam of light passed through it.

The sulphur dioxide is sometimes made by roasting sulphide ores for metallurgical processes, and sometimes by heating a mixture of native calcium sulphate, coal and coal ash (containing silica and alumina) in a cement furnace, the residue being cement clinker, and the carbon dioxide in the purified gas has no prejudicial effect on the contact process:

$$2CaSO_4 + C + (xSiO_2 + yAl_2O_3) = 2SO_2 + CO_2 + (2CaO, xSiO_2, yAl_2O_3).$$

In modern plants a catalyst of zeolite granules impregnated with vanadium pentoxide and ignited is used (Jaeger, *Ind. Eng. Chem.*, 1929, **21**, 627). The main part of the conversion is then carried out at a higher temperature, but in passing to the upper part of the catalyst mass, where the temperature is lower, the remaining sulphur dioxide in the gas is converted into trioxide.

In the **Badische process** the purified gas passes through an iron converter (Fig. 297) with vertical iron tubes packed with platinised asbestos. Twice the theoretical amount of oxygen (in the form of air) is present in the gas, which is preheated to start the reaction. By letting part of the incoming gas sweep over the outside of the hot tubes in which reaction occurs, no external heating is needed, since heat is evolved, and the process goes on continuously at 400°–450°.

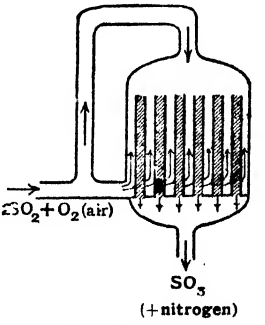


FIG. 297.—Badische converter.

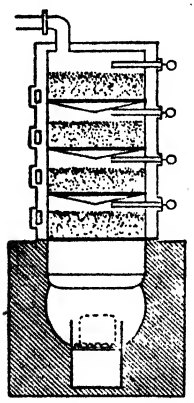


FIG. 298.—Schröder-Grillo converter.

In the **Schröder-Grillo process** the catalyst is prepared by moistening Epsom salt $MgSO_4$, $7H_2O$ with a solution of platinum chloride and heating in presence of sulphur dioxide. The salt loses water and swells to a voluminous contact mass on which the platinum is very finely divided. This is put on shelves in iron converters lagged outside (Fig. 298), and when the process is started it goes on without external heating.

The **Mannheim process** uses burnt pyrites (Fe_2O_3 and a little CuO) as the contact mass. This is filled into a rectangular tower, the lower part of which communicates with pyrites burners to which air dried in a sulphuric acid

tower is supplied (Fig. 299). The hot gas passes directly to the iron oxide shaft, and on account of the high temperature (over 600°) necessary with this catalyst only 60 p.c. of the SO_2 is converted into SO_3. The arsenious oxide in the burner gas remains in the oxide of iron as ferric arsenate, and after the SO_3 is absorbed from the exit gas by sulphuric acid, the gas is filtered through coke scrubbers soaked in concentrated sulphuric acid, reheated, and passed to a Tenteleff converter to finish the conversion. The **Tenteleff process** uses a catalyst of asbestos "sponge-cloths" which have been soaked in platinic chloride and reduced by formaldehyde. These are superposed in an iron frame, 3 ft. by 2 ft., in the gas current. The temperature is 450°–500°.

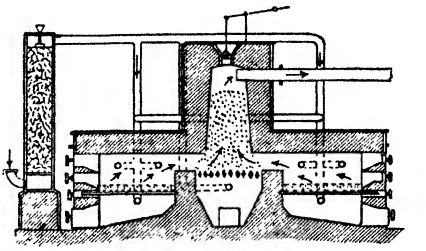


FIG. 299.—Mannheim contact process.

The sulphur trioxide cannot be absorbed from converter gas by passing through water, as a dense fog of sulphuric acid droplets is formed which cannot be condensed. The gas is passed into 97–99 p.c. sulphuric acid in iron towers, which rapidly absorbs the SO_3 to form fuming sulphuric acid, or if a regulated stream of water is admitted, the 97–99 p.c. acid is increased in quantity by the reaction $SO_3 + H_2O = H_2SO_4$ occurring in the liquid acid.

Fuming sulphuric acid is an oily liquid, colourless when pure, but coloured brown by organic matter. It emits thick white fumes in moist air. It may be kept in mild steel drums, but cracks cast iron (which resists ordinary concentrated sulphuric acid). It is made with different contents of free SO_3, *i.e.* SO_3 in excess of H_2SO_4.

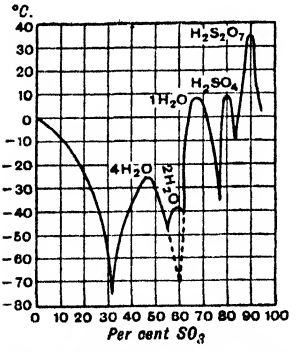


FIG. 300.—The system sulphur trioxide-water.

The strongest product contains 60 p.c. of free SO_3 and emits very dense fumes. The hydrates H_2O,SO_3 (H_2SO_4 or *monohydrate*, m.p. 10·49°), H_2SO_4,H_2O or $SO_3,2H_2O$ (m.p. 8·62°), $H_2O,2SO_3$ or $H_2S_2O_7$ (*disulphuric acid*, m.p. 35°), $H_2SO_4,2H_2O$, m.p. −38·9°, and $H_2SO_4,4H_2O$ (m.p. −29°) are shown on the freezing-point diagram (Fig. 300). Acids containing more than 60 and less than 40 p.c. of free SO_3 are liquid at the ordinary temperature, the others are solid.

The lead chamber process.—Sulphurous acid solution oxidises to sulphuric acid only very slowly in presence of oxygen; hydrogen peroxide oxidises it: $H_2O_2 + SO_2 = H_2SO_4$, but is too expensive, and chlorine gives a solution containing hydrochloric acid: $SO_2 + Cl_2 + 2H_2O = H_2SO_4 + 2HCl$. In presence of nitrogen dioxide or nitrous acid the reaction is rapid, and in presence of excess of atmospheric oxygen the nitrogen dioxide or nitrous acid is re-formed from the reduction product nitric oxide, which thus acts as a carrier of oxygen in a catalytic cycle.

EXPT. 10.—A dry 6-lit. flask (Fig. 301) is connected with wash-bottles containing concentrated sulphuric acid, through which oxygen, sulphur dioxide and nitric oxide can be passed, and a small flask *B* containing hot water. A rapid stream of oxygen is passed into *A*, then nitric oxide admitted, when red nitrogen dioxide is formed. Sulphur dioxide and nitric oxide are then admitted at about equal rates and after a short time the water in *B* is heated and oxygen bubbled through it. White fern-shaped crystals of nitrososulphuric acid form on the walls of *A*. The gas is swept out of *A* by a rapid current of dry oxygen (or air) and the water in *B* is boiled. When steam comes in contact with the crystals they dissolve with effervescence of red oxides of nitrogen and drops of sulphuric acid form, which trickle to the bottom of the flask. If insufficient water vapour is used in the first stage a white powdery deposit forms which gives purple droplets in contact with steam (" purple acid ").

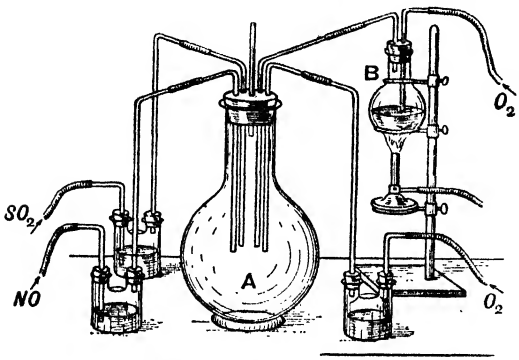


FIG. 301.—Experiment illustrating the chamber process.

Sulphuric acid (*oil of vitriol*) was made by Lemery (1675) by burning a mixture of sulphur and nitre (when SO_2 and NO_2 are formed) over a dish of water in a glass bell (*per campanem*), and the process was used on a small scale in 1740 by Ward at Richmond. Roebuck in 1746 used small lead chambers and these were gradually enlarged. Clement and Desormes in 1793 used a current of air through the chambers, and a continuous process in which sulphur dioxide formed in separate burners, air, steam and nitrous gases were passed through the chambers was introduced in 1810 by Holker into Chaptal's works in France. The Gay-Lussac (1827) and Glover (1859) towers were used from about the middle of the nineteenth century. The chamber process has been much improved and still holds its own for making acid of moderate concentration.

Clement and Desormes (1806) explained the catalytic action of the oxides of nitrogen on the intermediate compound theory (p. 144), and Berzelius (*Traité de Chimie*, 1830, **2**, 10) and Reynolds and Taylor (*J.S.C.I.*, 1912, **31**, 367) assumed the simple reactions ·

$$NO_2 + SO_2 + H_2O = NO + H_2SO_4$$
$$2NO + O_2 = 2NO_2.$$

Davy (1812) and Lunge (*J.C.S.*, 1885, **47**, 465) supposed that the intermediate compound is *nitrososulphuric acid* (" chamber crystals "), discovered by Clement and Desormes, which is alternately formed and decomposed by water :

$$2SO_2 + NO_2 + NO + O_2 + H_2O = 2SO_2(OH)\cdot O\cdot NO$$
$$2SO_2(OH)\cdot O\cdot NO + H_2O = 2SO_2(OH)_2 + NO_2 + NO.$$

In the first of a set of lead chambers, and in the Glover tower, the excess of sulphur dioxide present reacts with the nitrososulphuric acid :

$$2SO_2(OH)\cdot O\cdot NO + SO_2 + 2H_2O = 3SO_2(OH)_2 + 2NO.$$

Lunge and Berl (1906) modified this theory by assuming that a hypothetical " purple acid " H_2SNO_5 (p. 588) is the first product :

$$SO_2 + NO_2 + H_2O = H_2SNO_5$$
$$4H_2SNO_5 + O_2 = 4SO_2(OH)\cdot O\cdot NO + 2H_2O$$
$$2H_2SNO_5 + NO_2 = 2SO_2(OH)\cdot O\cdot NO + NO + H_2O,$$

and Raschig (1887) supposed this to be formed by the action of nitrous acid :

$$SO_2 + 2HNO_2 = H_2SNO_5 + NO$$
$$H_2SNO_5 = H_2SO_4 + NO.$$

The lead chamber plant (Fig. 302) consists of (i) pyrites (or sulphur) burners, (ii) a dust separator (if pyrites is used), (iii) a nitre oven (or ammonia oxidation apparatus), (iv) a Glover tower, (v) a series of lead chambers with arrangements for supplying steam or water spray, and (vi) a Gay-Lussac tower.

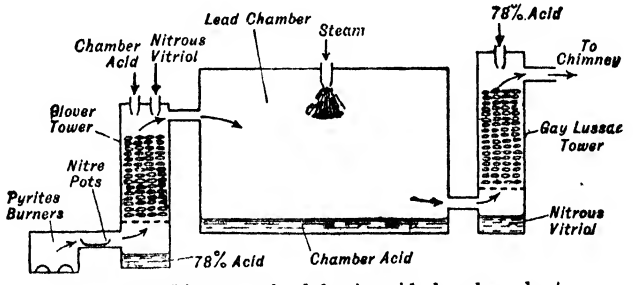


FIG. 302.—Diagram of sulphuric acid chamber plant.

The iron pyrites in lumps is burnt on grates in sets of brick furnaces (*pyrites burners*), the supply of air being regulated by sliding doors below and above the pyrites. Pyrites powder or " spent oxide " (p. 458) is burnt in vertical iron cylinders lined with firebrick, with a series of shelves, and the ore is raked from shelf to shelf by rotating scrapers until the burnt ore is discharged at the bottom. Sulphur is burnt in large inclined rotating cylinders or other special burners.

The burner gas (7 p.c. SO_2, 10 p.c. O_2, 83 p.c. N_2, by vol.) passes to a *dust-catcher* containing baffle-walls, and then through a *nitre-oven* in which pots containing sodium nitrate and sulphuric acid are placed to supply oxides of nitrogen to make up loss. In modern plants, the oxides of nitrogen are supplied by the oxidation of ammonia.

From the nitre-oven the hot gas passes into the *Glover tower*, a squat lead tower 20–30 ft. high and 6–8 ft. diameter lined with acid-resisting bricks and

packed with flints or earthenware shapes resting on an arch. Down this tower two streams of acid pass from tanks at the top, one supplying 65–70 p.c. acid from the lead chambers and the other 78 p.c. acid containing nitrososulphuric from the Gay-Lussac tower.

The functions of the Glover tower are: (*a*) to cool the burner gas to 50°–80°, (*b*) to "denitrate" the acid from the Gay-Lussac tower by dilution with chamber acid and heating, so setting the oxides of nitrogen again in circulation, and also forming about 25 p.c. of the total acid made, by reaction with sulphur dioxide in the burner gas, and (*c*) to concentrate the chamber acid to about 78 p.c. for use in the Gay-Lussac tower and for further concentration, or for sale, and at the same time provide some steam for the chambers.

The gas from the Glover tower passes by a large lead main to the large *lead chambers*, constructed of sheet lead weighing 6–8 lb. per sq. ft. They are oblong or square in shape, and dip into large lead trays with a seal of acid, being hung from wood or iron frames by lead straps welded on the sides by a hydrogen flame and without solder. Drum-shaped or polygonal (Mills-Packard) chambers, sometimes cooled by water flowing over the outside, are used, and sometimes even packed towers, but with these sufficient empty space must be provided to give time for reoxidation of NO to NO_2 in the gas.

Water is admitted as steam or usually a fine spray of liquid water from several jets in the roof of the chamber. Sulphuric acid is formed as a fog of fine drops which settle down as liquid *chamber acid* (65–70 p.c.) on the floor of the chamber. The conversion of SO_2 to H_2SO_4 reaches 98 p.c.

The gas from the last chamber, containing nitrogen, a little oxygen, most of the oxides of nitrogen in circulation, and a trace of sulphur dioxide, passes to the *Gay-Lussac tower*, a tall narrow tower lined with lead and packed with hard coke or earthenware shapes and fed with cold Glover tower acid (78 p.c.). Its function is to recover the oxides of nitrogen, which are absorbed to form *nitrous vitriol* containing nitrososulphuric acid equivalent to 1–2 p.c. of N_2O_3. This is pumped to the Glover tower for denitrification. The waste gas from the Gay-Lussac tower passes to a chimney or fan which maintains a draught through the whole system from the pyrites burners. In modern practice a high concentration of oxides of nitrogen ("circulating nitre"), with adequate Gay-Lussac tower capacity, is used, when the reactions proceed quickly, but with greater wear on the lead.

The chamber acid (65–70 p.c.) is used directly in making superphosphate of lime (p. 376). The 78 p.c. Glover tower acid is called "brown oil of vitriol" (B.O.V.) on account of its colour, due to impurities. Stronger acid (93–95 p.c.) is called "rectified oil of vitriol" (R.O.V.), and is made by further concentration in special apparatus in which the acid is heated and a current of hot air passed over its surface. The vapour emitted is of very weak acid, so that the liquid becomes concentrated.

In the **cascade process** the acid flows down a series of silica or silico-iron dishes resting on a kind of staircase of acid-resisting bricks, with the spout of

one basin discharging into the next lower basin. The acid is heated by a flue below and hot air sweeps over its surface. From the last dish, which may be of cast iron, the acid flows to a cooler.

In the **Kessler apparatus** the acid flows through a covered stone dish with ridges to bring the acid into intimate contact with hot gas from a coke furnace. The concentrated acid runs off to a cooler. The fumes enter a tower containing perforated plates down which the acid to be concentrated is fed. Much fume is condensed, and the temperature is such that steam escapes but sulphuric acid remains. In America hot gases from a burning spray of petroleum are bubbled through the acid.

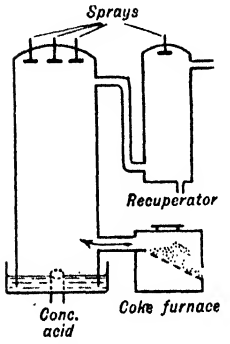


FIG. 303.—The Gaillard tower.

The **Gaillard tower** (Fig. 303) is an empty tower of stone or acid-resisting brick, from the top of which a fine spray of acid is discharged. In passing down the tower this meets a current of hot gas from a coke furnace. The acid is concentrated and runs out to a cooler. The fumes pass through a smaller empty lead tower called a *recuperator*, down which part of the acid to be concentrated is sprayed, and then to coke filters drenched with concentrated sulphuric acid.

The acid fumes from concentrators are passed through a chamber in which lead plates are hung, with lead-covered bars hanging vertically between them and charged to a potential of 20,000 volts. The acid droplets are attracted to the plates and the liquid runs to collecting tanks to be returned to the concentrators.

The most concentrated commercial acid (97–98 p.c.) is made by heating the 93–95 p.c. acid in pans by a direct fire. The 98 p.c. acid does not attack cast iron, whilst 93–95 p.c. acid dissolves it. The acid is run in a thin stream on the surface of 98 p.c. acid boiling in a large cast-iron pot with a siphon ("swan-neck") from which the concentrated acid runs continuously. The acid is more easily brought to the required strength by adding oleum, *i.e.* sulphuric acid containing free sulphur trioxide.

Commercial sulphuric acid made from pyrites contains arsenious oxide. It is purified by treatment with hydrogen sulphide (which also precipitates lead, copper and antimony) in lead towers or agitators. The precipitated arsenic sulphide is filtered by suction through porous earthenware plates, or removed by "flotation," when a little paraffin added floats to the surface of the liquid and carries the precipitate with it. Oxides of nitrogen are removed from the acid by heating strongly with a small amount of ammonium sulphate:

$$N_2O_3 + (NH_4)_2SO_4 = 2N_2 + H_2SO_4 + 3H_2O.$$

The lead sulphate present in commercial acid is deposited on dilution with water.

Pure sulphuric acid, sometimes called *monohydrate* ($H_2SO_4 = SO_3 + H_2O$), is made by adding sulphur trioxide to 98 p.c. acid. It is an oily liquid, fuming slightly in air from free SO_3 formed by dissociation: $H_2SO_4 \rightleftharpoons SO_3 + H_2O$. It freezes in ice and salt to crystals of m.p. 10·49°. On boiling, a constant-boiling acid (98·3 p.c. H_2SO_4) distils at 338°, usually given as the b.p. The

95 p.c. acid boils at 295°, emitting dense white suffocating fumes. The ordinary 98 p.c. acid is a colourless oily liquid, s. g. 1·84, which does not fume. It is very corrosive and has a strong affinity for water, on mixing with which it evolves much heat and the liquid may boil. The acid should always be poured into the water in a thin stream, with stirring. There is a contraction on mixing, which is a maximum for the composition $H_2SO_4 + 2H_2O$. If the acid is mixed with snow, cold is produced, as the latent heat of fusion of ice exceeds the evolution of heat on mixing the acid with liquid water.

The heats of solution (evolved) for 1 mol of SO_3 in n mols of water (Porter, *Trans. Faraday Soc.*, 1918, **13**, 373) are :

n - -	1	2	3	5	1600
k. cal. -	21·3	28·04	31·31	34·14	40·34

For a mols H_2SO_4 and b mols of water the heat evolved in g. cal. is given approximately by $17860b/(b + 1{\cdot}7983a)$.

The large evolution of heat and the contraction on mixing sulphuric acid and water point to a chemical change and many properties show maximum or minimum values at *approximately* whole molecular ratios of acid and water. This has been taken to imply definite hydrates in the *liquid* state, but the maxima and minima occur at different values for different properties (Pickering, *J.C.S.*, 1890, **57**, 64 ; Domke and Bein, *Z. anorg. Chem.*, 1905, **43**, 125 and bibl.). Such properties are : contraction (maximum, $H_2SO_4,2H_2O$), viscosity (max. H_2SO_4,H_2O and $H_2S_2O_7$; min. $3H_2SO_4,H_2O$), surface tension (max. $H_2SO_4,3H_2O$), compressibility (min. H_2SO_4,H_2O), index of refraction (max. H_2SO_4,H_2O and $H_2SO_4,2H_2O$), electrical conductivity (max. H_2SO_4,H_2O), and heat of solution (max. $H_2SO_4,2H_2O$) (Morgan and Davis, *J.A.C.S.*, 1916, **38**, 555).

The density of pure sulphuric acid at 15° is 1·8384, those of mixtures of the acid and water at 15° and of fuming sulphuric acid (" oleum ") containing free sulphur trioxide are given in the table. The 97·7 p.c. acid has a maximum density of 1·8414, and the density of oleum is a maximum for 60 p.c. of free SO_3.

Sulphuric Acid				Oleum	
H_2SO_4 p.c.	Density	H_2SO_4 p.c.	Density	Free SO_3 p.c.	Density
1·0	1·0061	60	1·5024	10	1·888
5	1·0332	65	1·5578	20	1·920
10	1·0681	70	1·6151	30	1·957
15	1·1045	75	1·6740	40	1·979
20	1·1424	80	1·7324	50	2·009
25	1·1816	85	1·7841	60	2·020
30	1·2220	90	1·8198	70	2·018
35	1·2636	95	1·8388	80	2·008
40	1·3065	97	1·8414	90	1·990
45	1·3514	98	1·8411	100	1·984
50	1·3990	99	1·8393		
55	1·4494	100	1·8384		

Concentrated sulphuric acid chars organic matter, removing the elements of water and leaving black carbon.

EXPT. 11.—To strong sugar syrup in a beaker standing in a stoneware trough add concentrated sulphuric acid and stir. The mixture becomes dark and froths to a black mass of carbon, steam and sulphur dioxide being evolved.

The vapour density of sulphuric acid at 444° corresponds with almost complete dissociation : $H_2SO_4 \rightleftharpoons SO_3 + H_2O$, but the products recombine on cooling. When the acid is heated in an open flask the steam diffuses more rapidly and the liquid is enriched in SO_3 (Wanklyn and Robinson, 1863). If the acid vapour is passed through a strongly heated platinum or quartz tube it decomposes into oxygen, sulphur dioxide and steam, which do not recombine on cooling : $2H_2SO_4 = 2SO_2 + O_2 + 2H_2O$. This also occurs if the acid is dropped into a red-hot platinum flask.

Sulphuric acid ionises in two stages, the first nearly complete but the second appreciable only at high dilution (Sherril and Noyes, *J.A.C.S.*, 1926, **48**, 1861) :

$$(1)\ H_2SO_4 \rightleftharpoons H^{\cdot} + HSO_4'\ ; \quad (2)\ HSO_4' \rightleftharpoons H^{\cdot} + SO_4''.$$

The acid and normal sulphates are $MHSO_4$ and M_2SO_4 (M univalent), but disulphates $M_2S_2O_7$ and more complex sulphates, formed from normal sulphates and sulphur trioxide, M_2SO_4,xSO_3, are known. Many normal sulphates occur as minerals : gypsum $CaSO_4,2H_2O$, anhydrite $CaSO_4$, celestine $SrSO_4$, barytes $BaSO_4$, glauberite $CaSO_4,Na_2SO_4$, and kieserite $MgSO_4,H_2O$ are some examples. Many sulphates are soluble and crystalline, but calcium, strontium and lead sulphates are sparingly soluble, and barium sulphate is almost insoluble in water and dilute acids.

Sulphuric acid is only very slowly reduced by hydrogen in the cold (not appreciably at 0°) but more rapidly on heating : $H_2SO_4 + H_2 = SO_2 + 2H_2O$. Carbon, sulphur (p. 700) and phosphorus reduce the hot acid :

$$2P + 3H_2SO_4 = 2H_3PO_3 + 3SO_2.$$

Many metals (Mg, Zn, Fe, etc.) dissolve in *dilute* sulphuric acid with evolution of hydrogen. Sodium, potassium and magnesium liberate hydrogen from the cold *concentrated* acid. Most metals dissolve in the hot concentrated acid with evolution of sulphur dioxide (Muir and Adie, *J.C.S.*, 1888, **53**, 47 ; Berthelot, *Ann. Chim.*, 1898, **14**, 176 ; Adie, *Proc. Chem. Soc.*, 1899, **15**, 132 ; Fawsitt and Powell, *J.S.C.I.*, 1914, **33**, 234). Iron gives hydrogen and sulphur dioxide but the action soon stops ; zinc gives sulphur dioxide with concentrated acid, but a mixture of 4 vols. of conc. acid and 1 vol. of water gives hydrogen sulphide and a little sulphur : $4Zn + 5H_2SO_4 = 4ZnSO_4 + H_2S + 4H_2O$; lead is attacked by hot very concentrated acid (pure lead is more resistant), and tin and antimony are dissolved.

The reduction to sulphur dioxide by metals has been represented by two sets of equations, in which M is a bivalent metal :

$$(1)\quad H_2SO_4 + M = MSO_4 + H_2$$
$$H_2SO_4 + H_2 = 2H_2O + SO_2.$$
$$(2)\quad H_2SO_4 + M = MO + SO_2 + H_2O$$
$$H_2SO_4 + MO = MSO_4 + H_2O.$$

Alkali metal (except ammonium), lead, and magnesium sulphates are stable on heating, except at very high temperatures ; zinc, copper and iron sulphates at high temperatures evolve SO_3, SO_2 and oxygen ; calcium sulphate is decomposed at a high temperature, strontium and barium sulphates are stable. Most sulphates are reduced to sulphides by heating in a current of hydrogen or with carbon :

$$K_2SO_4 + 4H_2 = K_2S + 4H_2O$$
$$Na_2SO_4 + 2C = Na_2S + 2CO_2$$
$$BaSO_4 + 4C = BaS + 4CO.$$

On heating in hydrogen silver sulphate is reduced to the metal :

$$Ag_2SO_4 + 2H_2 = 2Ag + SO_2 + 2H_2O,$$

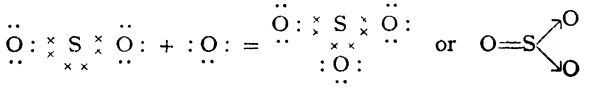
aluminium and chromium sulphates form the oxides :

$$Al_2(SO_4)_3 + 3H_2 = Al_2O_3 + 3SO_2 + 3H_2O.$$

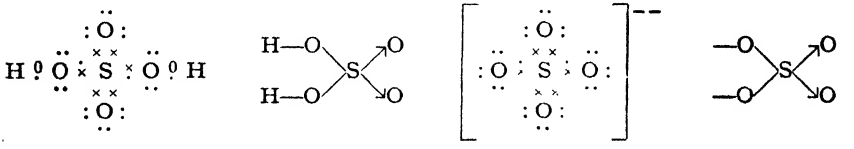
Many sulphates are decomposed when heated in a current of hydrogen chloride :

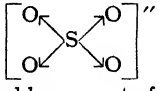
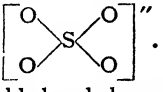
$$2CuSO_4 + 4HCl = 2CuCl_2 + 2SO_2 + 2H_2O + O_2.$$

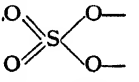
The electronic formula of sulphur trioxide may be written by adding an atom of oxygen to the lone pair of electrons on the sulphur in the dioxide (p. 702) :



Sulphuric acid and the sulphate ion are represented as :



but as the sulphate ion may be supposed formed from the sulphur ion $\left[: \ddot{S} : \right]''$ donating four electron pairs to four neutral oxygen atoms, and as there is no real difference between the two kinds of covalent links, it could equally well be written  or  . The bond distances, however, show a considerable amount of double bond character in the links, so that these formulae are too naïve and the actual state is a resonance hybrid, the old formula :



with the double bonds resonating among the oxygen atoms, making them equivalent, and with bonds supposed to have partial ionic character, being more

satisfactory (Pauling, *The Nature of the Chemical Bond*, 1940, 239). In what follows the now conventional formulae with coordinate links will be used on this understanding.

The chlorides of sulphuric acid.—By the action of phosphorus pentachloride on concentrated sulphuric acid $SO_2(OH)_2$, the two hydroxyl groups can be successively replaced by chlorine, forming **chlorosulphonic acid** $SO_2(OH)Cl$, and **sulphuryl chloride** SO_2Cl_2. The reaction is a general one with oxyacids, the acid chloride, phosphorus oxychloride and hydrogen chloride being formed :

$$SO_2(OH)_2 + PCl_5 = \underset{\text{b p. 151°}}{SO_2(OH)Cl} + \underset{\text{b.p. 107·3°}}{POCl_3} + HCl$$

$$SO_2(OH)Cl + PCl_5 = \underset{\text{b.p. 69·1°}}{SO_2Cl_2} + POCl_3 + HCl.$$

The boiling points show that the products can be separated by fractional distillation. Since excess of phosphorus pentachloride gives sulphuryl chloride, chlorosulphonic acid may be prepared with phosphorus oxychloride, which does not act further on it :

$$2SO_2(OH)_2 + POCl_3 = 2SO_2(OH)Cl + HPO_3 + HCl.$$

Chlorosulphonic acid (Williamson, 1855) is formed by direct combination of sulphur trioxide and hydrogen chloride : $SO_3 + HCl = HClSO_3$, and is made on the large scale by passing dry hydrogen chloride into fuming sulphuric acid (containing SO_3) and distilling. It is a colourless fuming liquid, s. g. 1·753 at 20°, which is hydrolysed by water with dangerous violence :

$$SO_2(OH)Cl + H_2O = SO_2(OH)_2 + HCl.$$

Its vapour at 170°–180° is decomposed into sulphuryl chloride and sulphuric acid : $2SO_3HCl = SO_2Cl_2 + H_2SO_4$, and at higher temperatures into chlorine, sulphur dioxide and steam. It reacts violently with silver nitrate, forming nitrososulphuric acid :

$$2SO_2(OH)Cl + 2AgNO_3 = 2AgCl + 2SO_2(OH)O{\cdot}NO + O_2.$$

A sodium salt is formed by the action of sodium chloride on the acid :

$$SO_2(OH)Cl + NaCl = SO_2(ONa)Cl + HCl.$$

Sulphuryl chloride (Regnault, 1838) is formed by direct combination of sulphur dioxide and chlorine in sunlight or in presence of catalysts such as charcoal, camphor, or acetic anhydride : $SO_2 + Cl_2 = SO_2Cl_2$. It is formed by heating chlorosulphonic acid in a sealed tube at 180°, or with a little mercuric sulphate, antimony or tin as a catalyst, in a flask at 70° under a reflux condenser : $2SO_3HCl = SO_2Cl_2 + H_2SO_4$. It is a colourless fuming liquid, s. g. 1·667 at 20°, b.p. 69·1° without decomposition ; the vapour is much dissociated at 330° (Smith, *J.A.C.S.*, 1925, **47**, 1862) : $SO_2Cl_2 \rightleftharpoons SO_2 + Cl_2$. The liquid is rather slowly hydrolysed by water : $SO_2Cl_2 + 2H_2O = SO_2(OH)_2 + 2HCl$, and chlorosulphonic acid is formed as an intermediate stage : $SO_2Cl_2 + H_2O = SO_2(OH)Cl + HCl$.

With ice-cold water it forms a crystalline hydrate $SO_2Cl_2,15H_2O$. A solution of sulphuryl chloride in petrol is used to make wool unshrinkable: it breaks some linkages in the spiral fibre molecules.

The chloride of disulphuric acid, **disulphuryl chloride** (or *pyrosulphuryl chloride*) $S_2O_5Cl_2$, is obtained by the action of sulphur trioxide on thionyl chloride or preferably on sulphur chloride (Rose, 1838):

$$SOCl_2 + 2SO_3 = S_2O_5Cl_2 + SO_2$$
$$5SO_3 + S_2Cl_2 = 5SO_2 + S_2O_5Cl_2.$$

It is formed by the action of sulphur trioxide or chlorosulphonic acid on phosphorus pentachloride:

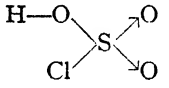
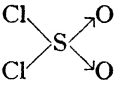
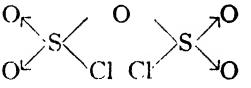
$$2SO_3 + PCl_5 = POCl_3 + S_2O_5Cl_2$$
$$2SO_2(OH)Cl + PCl_5 = POCl_3 + 2HCl + S_2O_5Cl_2,$$

and by dropping fuming sulphuric acid into hot carbon tetrachloride:

$$3CCl_4 + 2H_2SO_4 = 3COCl_2 + S_2O_5Cl_2 + 4HCl.$$

It is a heavy mobile liquid, s. g. 1·844/18°, boiling at 57°/30 mm., or 150·7°/730 mm., giving a nearly normal vapour density, although some decomposition into sulphur dioxide, sulphur trioxide and chlorine occurs: $S_2O_5Cl_2 = SO_2 + SO_3 + Cl_2$. It fumes only slightly and is decomposed only slowly by water: $S_2O_5Cl_2 + 3H_2O = 2H_2SO_4 + 2HCl$.

The conventional formulae of the chlorides of sulphuric and disulphuric acids follow from those of the acids (see p. 715):

Fluosulphonic acid $SO_2(OH)F$, formed by distilling fluorspar with fuming sulphuric acid in an iron retort: $SO_3 + HF = SO_2(OH)F$, is a colourless mobile liquid, b.p. 162·6°, the vapour being stable at 900°. The acid is incompletely hydrolysed by water: $SO_2(OH)F + H_2O \rightleftharpoons SO_2(OH)_2 + HF$, and very stable salts are formed from sulphur trioxide and alkali fluorides: $SO_3 + NaF = SO_2(ONa)F$.

Sulphuryl fluoride SO_2F_2 is formed by passing heated fluorine into excess of sulphur dioxide. $SO_2 + F_2 = SO_2F_2$, or more conveniently by heating barium fluosulphonate; $Ba(SO_3F)_2 = BaSO_4 + SO_2F_2$. It is a colourless stable inert gas, b.p. −52°, m.p. −120°, sparingly soluble in water, and is decomposed by sodium only at a high temperature, but is decomposed by alkali solution:

$$SO_2F_2 + 4NaOH = Na_2SO_4 + 2NaF + 2H_2O.$$

Sulphamide and sulphimide.—The action of ammonia gas on a solution of sulphuryl chloride in dry benzene forms *sulphamide* $SO_2(NH_2)_2$ (Regnault, 1838):

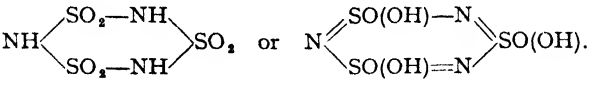
$$SO_2Cl_2 + 4NH_3 = SO_2(NH_2)_2 + 2NH_4Cl.$$

It is purified by decomposing the silver compound $SO_2(NHAg)_2$ with hydrochloric acid and forms large colourless crystals (Mann, *J.C.S.*, 1933, 412).

Sulphimide is polymerised $(SO_2{=}NH)_3$; it is formed by heating sulphamide at 180° till ammonia is no longer evolved (Traube, 1892):

$$3SO_2(NH_2)_2 = (SO_2{=}NH)_3 + 3NH_3.$$

It is purified by decomposing the silver compound $(SO_2{=}NAg)_3$ with hydrochloric acid, and forms colourless crystals. It probably has a ring structure :



Higher Oxides of Sulphur

By the action of a silent discharge on a mixture of sulphur dioxide and oxygen Berthelot (1878) found a contraction, and a viscous liquid separated on the walls of the ozoniser, solidifying at 0° to long prismatic crystals, the analysis of which gave the formula S_2O_7, *persulphuric anhydride*. These gave an oxidising solution of persulphuric acid with water. Meyer, Bailleul and Henkel (1922) and Maisin (1928) found that the prolonged action of the discharge gave $SO_3{,}2SO_4$, and Schwarz and Achenbach (1934) reported that with a glow discharge at low pressure and cooling the gas with liquid air, white solid **sulphur tetroxide** SO_4 separated, melting at 0° to oily drops of S_2O_7.

Persulphuric Acids

Faraday (1834) when electrolysing a concentrated solution of sulphuric acid noticed " a remarkable disappearance of oxygen." He thought this was due to the formation of hydrogen peroxide, but this was disproved by Brodie (1864), who suggested that persulphuric acid H_2SO_5 is formed. Marshall (*Proc. R.S. Edin.*, 1890, **18**, 63 ; *J.C.S.*, 1891, **59**, 771) found that on electrolysis of concentrated potassium hydrogen sulphate solution crystals of the composition KSO_4 separate at the anode.

Bredig (1893) from Ostwald's conductivity rule (p. 149) showed that the formula is $K_2S_2O_8$ and hence persulphuric acid is dibasic, and Moeller (1893) calculated van't Hoff's factor i (p. 80) from the freezing points of potassium persulphate solutions and showed that the degree of dissociation $\alpha = (i-1)/(n-1)$ agrees with the conductivity value $\alpha = \lambda/\lambda_\infty$ when $n = 3$ ($K_2S_2O_8 = 2K^{\cdot} + S_2O_8''$).

In Marshall's experiment the HSO_4' ions discharged at the anode form persulphuric acid : $2HSO_4 = H_2S_2O_8$ and sparingly soluble potassium persulphate crystallises : $H_2S_2O_8 + 2KHSO_4 = K_2S_2O_8 + 2H_2SO_4$. Another explanation is that the HSO_4' ions are oxidised by nascent oxygen at the anode : $2HSO_4' + H_2O + O = H_2S_2O_8 + 2OH'$.

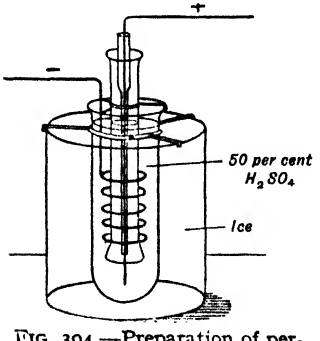


Fig. 304.—Preparation of persulphuric acid.

Expt. 12.—Persulphuric acid is formed by the electrolysis of 50 p.c. sulphuric acid with an anode of platinum wire surrounded by a glass tube to serve as a diaphragm. The cathode is a spiral of copper wire outside the diaphragm (Fig. 304). The apparatus is immersed in ice. The addition of a little hydrochloric acid promotes the reaction. If a saturated potassium

hydrogen sulphate solution is used crystals of the persulphate separate out. The solution in each experiment gives a brown colour with potassium iodide: $S_2O_8'' + 2I' = 2SO_4'' + I_2$.

Ammonium persulphate $(NH_4)_2S_2O_8$ is much more soluble than the potassium salt and is made commercially by electrolysis of a solution of ammonium sulphate in sulphuric acid.

Potassium persulphate decomposes on heating: $2K_2S_2O_8 = 2K_2SO_4 + 2SO_3 + O_2$, and the solution evolves ozonised oxygen slowly in the cold and rapidly on heating: $2K_2S_2O_8 + 2H_2O = 4KHSO_4 + O_2$.

Persulphates are powerful oxidising agents liberating iodine from potassium iodide, oxidising ferrous to ferric salts: $2Fe'' + S_2O_8'' = 2Fe''' + 2SO_4''$, and converting chromic salts to dichromates and manganous salts to permanganates by boiling in presence of silver nitrate as a catalyst (Marshall, 1901; Yost, *J.A.C.S.*, 1926, **48**, 152). In presence of alkali, manganous, cobalt, nickel and lead salts form peroxides: $Mn(OH)_2 + K_2S_2O_8 + H_2O = MnO_2 + 2KHSO_4 + H_2O$. Potassium (but not ammonium) persulphate precipitates black argentic oxide $Ag^{II}O$ from silver nitrate solution:

$$K_2S_2O_8 + 2AgNO_3 + 2H_2O = 2AgO + 2KHSO_4 + 2HNO_3.$$

Many metals dissolve in persulphate solutions: $Zn + K_2S_2O_8 = ZnSO_4 + K_2SO_4$.

Ammonium persulphate is used for bleaching and for "reducing" the intensity of photographic negatives. Barium persulphate BaS_2O_8 is very soluble (separation from sulphuric acid); on boiling the solution deposits barium sulphate.

A solution of a new persulphuric acid, H_2SO_5, which is a powerful oxidising agent, was obtained by Caro (1898) by grinding potassium persulphate with concentrated sulphuric acid, allowing to stand for an hour, and pouring on ice:

$$H_2S_2O_8 + H_2O = H_2SO_4 + H_2SO_5.$$

It oxidises aniline to nitrosobenzene and nitrobenzene. Baeyer and Villiger (*Ber.*, 1901, **34**, 853) separated free sulphuric acid from the solution by shaking with barium phosphate: $Ba_3(PO_4)_2 + 3H_2SO_4 = 3BaSO_4 + 2H_3PO_4$, and differentiated Marshall's acid ($H_2S_2O_8$), Caro's acid (H_2SO_5) and hydrogen peroxide by the reactions:

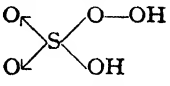
1. Caro's acid instantly liberates iodine from iodides.
2. Marshall's acid only slowly liberates iodine from iodides.
3. Hydrogen peroxide at once reduces potassium permanganate, which is not changed by persulphuric acids.

In the solution of Caro's acid the ratio SO_3 : peroxide O was found to be 1 : 1, hence the formula is $SO_3 + O + H_2O$ or H_2SO_5, **permonosulphuric acid.** This was prepared nearly pure by Ahrle (1909) by the action of sulphur trioxide on very concentrated hydrogen peroxide: $SO_3 + H_2O_2 = H_2SO_5$. The reaction with concentrated sulphuric acid is reversible: $H_2SO_4 + H_2O_2 \rightleftharpoons H_2SO_5 + H_2O$. D'Ans and Friederich (1910) prepared pure permonosulphuric acid and per-

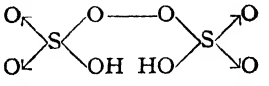
disulphuric acid $H_2S_2O_8$ by the action of anhydrous hydrogen peroxide on chlorosulphonic acid :

$$HO{\cdot}SO_2{\cdot}Cl + HO{\cdot}OH = HO{\cdot}SO_2{\cdot}O{\cdot}OH + HCl$$
$$HO{\cdot}SO_2{\cdot}Cl + HO{\cdot}O{\cdot}SO_2{\cdot}OH = HO{\cdot}SO_2{\cdot}O{\cdot}O{\cdot}SO_2{\cdot}OH + HCl.$$

These reactions give the conventional structural formulae :



and



The S_2O_8'' ion consists of two tetrahedral SO_4 groups joined by an oblique covalent bond (Zachariasen and Mooney, 1934).

Permonosulphuric acid is crystalline, melts at 45°, and is stable for some days. Perdisulphuric acid forms crystals stable up to 60°, but in solution slowly passes into permonosulphuric acid and sulphuric acid : $H_2O + H_2S_2O_8 = H_2SO_4 + H_2SO_5$.

No solid salts of H_2SO_5 are known, but a solution of $KHSO_5$ is said to be formed by the action of H_2O_2 on $KClSO_3$ (p. 716) : the acid should be monobasic.

Thiosulphuric Acid

Free thiosulphuric acid $H_2S_2O_3$ is not known, except possibly in solution, as it rapidly decomposes with separation of sulphur : $H_2S_2O_3 = H_2SO_3 + S$ (Colefax, *J.C.S.*, 1892, **61**, 176), but by boiling sulphur with an alkali sulphite solution this reaction is reversed and a solution of thiosulphate formed : $Na_2SO_3 + S = Na_2S_2O_3$. The sodium salt, discovered by Chaussier in 1799, forms large monoclinic crystals $Na_2S_2O_3{,}5H_2O$, commonly called " sodium hyposulphite " or " hypo " and used in photography and as an antichlor (Hargreaves and Dunningham, *J.S.C.I.*, 1923, **42**, 147 T). The stability in solution is increased by using boiled sterilised water, and adding acid sulphite ($Na_2S_2O_5$), or in volumetric solutions 0·2 g. of Na_2CO_3 per lit. (Kilpatrick, *J.A.C.S.*, 1923, **45**, 2132).

Pure sodium thiosulphate, and especially potassium thiosulphate $K_2S_2O_3$, $\frac{5}{3}H_2O$, are best prepared by the interaction of alkali hydrogen sulphides and hydrogen sulphites in solution, and crystallising (Foerster and Mommsen, *Ber.*, 1924, **57**, 258) : $2KHS + 4KHSO_3 = 3K_2S_2O_3 + 3H_2O$.

Thiosulphuric acid may be regarded (Odling, 1855) as sulphuric acid in which a hydroxyl group OH is replaced by a sulphydryl group SH, viz. $HS{\cdot}SO_2{\cdot}OH$ (the acid $HS{\cdot}SO_2{\cdot}SH$ is unknown). Spring showed that sodium thiosulphate solution is reduced by sodium amalgam to sulphite and sulphide : $NaO{\cdot}SO_2{\cdot}SNa + 2Na = NaO{\cdot}SO_2{\cdot}Na + Na_2S$, and Bunte (1874) that ethyl sodium thiosulphate (formed by the action of ethyl bromide on a concentrated solution of sodium thiosulphate : $Na_2S_2O_3 + C_2H_5Br = C_2H_5NaS_2O_3 + NaBr$), on warming with concentrated hydrochloric acid, forms mercaptan C_2H_5SH, in which the ethyl group is known to be attached to sulphur (p. 704) :

$$NaO{\cdot}SO_2{\cdot}SC_2H_5 + HOH = NaO{\cdot}SO_2{\cdot}OH + C_2H_5SH.$$

Thiosulphates and sulphides are formed by the action of alkalis on sulphur, and the reaction may be *formally* represented as a hydrolysis in which an intermediate oxide SO is formed (cf. p. 598) :

$$2S + 2OH' = SO + S'' + H_2O$$
$$2SO + 2OH' = S_2O_3'' + H_2O$$
$$\therefore\ 4S + 6OH' = 2S'' + S_2O_3'' + 3H_2O.$$

With excess of sulphur, yellow solutions containing *polysulphides* are formed: $S'' + nS = S_{n+1}''$; these also result from the oxidation of sulphide solutions by atmospheric oxygen, sulphur being also precipitated in the case of ammonium and alkaline earth sulphides: $2S'' + O_2 + 2H_2O = 2S + 4OH'$ and $S'' + nS = S_{n+1}''$; with excess of oxygen thiosulphate and sulphate are formed. The actual reactions are hence rather complex:

$$4S + 6NaOH = 2Na_2S + Na_2S_2O_3 + 3H_2O$$
$$12S + 3Ca(OH)_2 = 2CaS_5 + CaS_2O_3 + 3H_2O$$
$$12CaS + 9H_2O + 6O_2 = 9Ca(OH)_2 + CaS_2O_3 + 2CaS_5$$
$$2CaS_5 + 3O_2 = 2CaS_2O_3 + 6S.$$

Thiosulphate is formed on passing sulphur dioxide into sulphide solutions:

$$2Na_2S + 3SO_2 = 2Na_2S_2O_3 + S,$$

or sulphur dioxide or oxygen over heated sulphides or hydrosulphides:

$$2NaHS + 2O_2 = Na_2S_2O_3 + H_2O.$$

On fusing sulphur with alkalis or alkali carbonates, a dark brown mass (*liver of sulphur*) is formed. The first reactions are probably:

$$4S + 3K_2CO_3 = 2K_2S + K_2S_2O_3 + 3CO_2$$
$$K_2S + 3S = K_2S_4,$$

but much of the thiosulphate is decomposed at higher temperature:

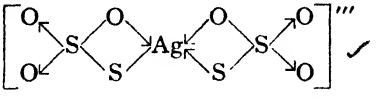
$$4K_2S_2O_3 = 3K_2SO_4 + K_2S_5,$$

so that the final reaction is approximately

$$16S + 12K_2CO_3 = 8K_2S + K_2S_5 + 3K_2SO_4 + 12CO_2.$$

Sodium thiosulphate crystals melt at 48°, lose water at 215°, and above 223° decompose into sulphate and pentasulphide: $4Na_2S_2O_3 = 3Na_2SO_4 + Na_2S_5$. At higher temperatures the Na_2S_5 loses some sulphur: $Na_2S_5 = Na_2S_4 + S$ (K_2S_5 is stable).

Most thiosulphates, except those of alkali metals, are sparingly soluble but dissolve in alkali thiosulphate solutions forming complex anions. Sodium thiosulphate solution also dissolves silver halides (AgCl,AgBr,AgI) forming a complex ion $Ag(S_2O_3)_2'''$ or



which has a sweet taste. Thiosulphate solution is used as a "fixing" agent in photography, as it dissolves unaltered silver halides (p. 352). The free acid $H[Ag(S_2O_3],H_2O$ is precipitated by concentrated nitric acid from a solution of $Na[Ag(S_2O_3]$ in ammonia (Baines, *J.C.S.*, 1929, 2763).

White precipitates of thiosulphates of silver, lead and mercury soon blacken from formation of sulphides :

$$SO_2(OAg)(SAg) + H_2O = SO_2(OH)_2 + Ag_2S.$$

The yellow cuprous salt $Na_4[Cu_6(S_2O_3)_5],6H_2O$, which crystallises from solutions of a cupric salt and sodium thiosulphate, decomposes on boiling to copper sulphides and sulphur. Cupric thiosulphate, however, exists as a coordination compound with ethylenediamine $[Cu\ en_2]S_2O_3$.

Thiosulphates are oxidised by chlorine and bromine water, and sulphur is precipitated (sodium thiosulphate is used as an *antichlor* to remove excess of chlorine from bleached fabrics) :

$$Na_2S_2O_3 + Cl_2 + H_2O = Na_2SO_4 + S + 2HCl,$$

but with a large excess of halogen the sulphur is slowly oxidised to sulphuric acid :

$$Na_2S_2O_3 + 4Cl_2 + 5H_2O = 2NaCl + 2H_2SO_4 + 6HCl,$$

some trithionate and tetrathionate being also formed. Iodine reacts differently, giving a *quantitative* yield of tetrathionate :

$$2Na_2S_2O_3 + I_2 = 2NaI + Na_2S_4O_6.$$

Potassium permanganate in *neutral* solution forms sulphate :

$$Na_2S_2O_3 + 2KMnO_4 = Na_2SO_4 + K_2SO_4 + Mn_2O_3,$$

but in *acid* solution some dithionate $Na_2S_2O_6$ is also formed.

Hyposulphurous Acid

This acid $H_2S_2O_4$ must not be confused with thiosulphuric acid (formerly called hyposulphurous acid) ; it is sometimes called *hydrosulphurous acid* and the name *dithionous acid* has been proposed.

On passing sulphur dioxide into a suspension of zinc dust in absolute alcohol the metal dissolves without evolution of hydrogen and a solution of zinc hyposulphite (which can be crystallised) is formed : $Zn + 2SO_2 = ZnS_2O_4$. The filtered solution at once bleaches indigo and is a powerful reducing agent. The sodium salt is formed by the action of sulphur dioxide diluted with hydrogen (the pure gas causes explosion) on sodium hydride (Moissan, 1902) : $2NaH + 2SO_2 = Na_2S_2O_4 + H_2$, but is usually prepared by reducing an acid sulphite with zinc : $2NaHSO_3 + SO_2 + Zn = Na_2S_2O_4 + ZnSO_3 + H_2O$.

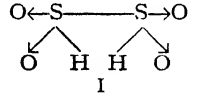
Zinc dust is added to a cooled concentrated solution of $NaHSO_3$ in a corked flask and sulphur dioxide passed in. Milk of lime is added to precipitate the zinc sulphite : $ZnSO_3 + Ca(OH)_2 = Zn(OH)_2 + CaSO_3$, and the filtrate is saturated with sodium chloride. The thin glassy prisms of $Na_2S_2O_4,2H_2O$ which separate oxidise rapidly to sulphite in air ; they are washed with aqueous and then anhydrous acetone and dried in a desiccator over concentrated sulphuric acid, when a white powder of $Na_2S_2O_4$ remains. (For purification, see Christiansen and Norton, *Ind. Eng. Chem.*, 1929, **14**, 1126.)

On the large scale sulphur dioxide is passed into a cooled suspension of zinc dust in water, the ZnS_2O_4 solution precipitated with sodium carbonate: $ZnS_2O_4 + Na_2CO_3 = ZnCO_3 + Na_2S_2O_4$, and the filtrate saturated with common salt, when needle-shaped crystals of $Na_2S_2O_4,2H_2O$ separate. The suspension is heated rapidly to 60° when a crystalline powder of $Na_2S_2O_4$ settles, which is washed with alcohol and dried in vacuum. The product contains 90 p.c. of $Na_2S_2O_4$ and some NaCl. It is fairly stable in air. In solution the hyposulphite decomposes to disulphite and thiosulphate (Jellinek, 1919): $2Na_2S_2O_4 = Na_2S_2O_5 + Na_2S_2O_3$.

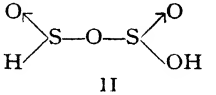
Sodium hyposulphite was prepared in 1869 by Schützenberger, who formulated it as $NaHSO_2$. The correct formula was established by Bernthsen (1881), who showed that for every two atoms of sulphur, *one* of oxygen is required to form a sulphite (by ammoniacal copper sulphate), and *three* atoms to form a sulphate (by a solution of iodine). These results agree with the formula S_2O_3 for the anhydride (H_2O,S_2O_3), but not with SO, formerly accepted ($H_2SO_2 = H_2O,SO$):

$$S_2O_3 + O = 2SO_2 \qquad 2SO + 2O = 2SO_2$$
$$S_2O_3 + 3O = 2SO_3 \qquad 2SO + 4O = 2SO_3.$$

The structural formula I is usually adopted, although II and III have also been proposed:



I



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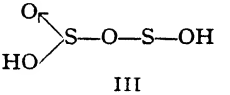


III

Formula I accounts for the great reducing power, two hydrogen atoms linked to sulphur being present, and for the formation of some dithionate on oxidation. The doubled formula $H_2S_2O_4$ (not HSO_2) is proved by the diamagnetism of the ion S_2O_4'' (Klemm, 1937).

The free acid is supposed to be present in the yellow solution of $Na_2S_2O_4$ and oxalic acid but it rapidly decomposes into sulphurous acid and sulphur, and the colour may be due to SO (p. 721): $2SO = SO_2 + S$.

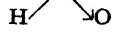
Sodium hyposulphite is a very powerful reducing agent and is used to dissolve indigo (or other vat dyes) by forming reduced solutions:

$$Na_2S_2O_4 + 2H_2O = 2NaHSO_3 + 2H \text{ (nascent)}.$$

Instead of sodium hyposulphite the stable reaction product with formaldehyde, called *rongalite* C, is often used in reducing dyes. This contains a formaldehyde compound of *sodium sulphoxylate* Na_2SO_2:

$$Na_2S_2O_4 + H_2O = NaHSO_2 + NaHSO_3$$
$$NaHSO_2 + NaHSO_3 + 2H{\cdot}COH = NaHSO_2(H{\cdot}COH) + NaHSO_3(H{\cdot}COH).$$

It can be made in this way or by reducing $NaHSO_3$ solution with zinc in presence of formaldehyde. The salt $NaHSO_2(H{\cdot}COH),2H_2O$ can be separated by crystallisation.

Sulphoxylic acid is usually formulated as  .

Sodium hyposulphite solution reacts with hydrogen sulphide (Sinnatt, 1914): $Na_2S_2O_4 + H_2S = Na_2S_2O_3 + H_2O + S$, and with ferricyanide (Christiansen and Norton, 1922): $2Fe(CN)_6''' + S_2O_4'' = 2Fe(CN)_6'''' + 2SO_2$, and both reactions may be used for its determination.

Thionic Acids

The thionic acids form a group with the general formula $H_2S_nO_6$, where n is 2, 3, 4, 5 and 6. They are known only in solution but form crystalline salts. Some authors separate dithionic acid $H_2S_2O_6$ from the " true " thionic acids.

The methods of preparation are readily comprehended if it is assumed that: (i) sulphur dioxide or acid sulphite solutions contain the ion S_2O_5'' (p. 703), (ii) acid thiosulphate solutions contain the radical SO: $S_2O_3'' + 2H^+ = 2SO + H_2O$.

A *dithionate* is formed by oxidation of sulphur dioxide or acid sulphite solution: $S_2O_5'' + O = S_2O_6''$; a *trithionate* by the action of sulphurous acid on a thiosulphate: $S_2O_3'' + 2H^+ = 2SO + H_2O$ and $SO + S_2O_5'' = S_3O_6''$; a *tetrathionate* by oxidation of a thiosulphate: $2S_2O_3'' = S_4O_6'' + 2e$; and a solution of *pentathionic acid* by the action of hydrogen sulphide on sulphurous acid: $H_2S + 2SO_2 = 3SO + H_2O$ and $5SO + H_2O = H_2S_5O_6$.

Dithionic acid $H_2S_2O_6$, discovered by Gay-Lussac and Welter in 1819, is formed by the action of mild oxidising agents, such as a suspension of manganese dioxide, on sulphurous acid (Bassett and Henry, *J.C.S.*, 1935, 914): $S_2O_5'' + O = S_2O_6''$.

Expt. 13.—Sulphur dioxide is slowly passed into a suspension of *finely ground* crystalline native manganese dioxide (*pyrolusite*) in water, cooled in ice. Manganous dithionate and some manganous sulphate are formed: $MnO_2 + 2SO_2 = MnS_2O_6$; $MnO_2 + SO_2 = MnSO_4$. When all the pyrolusite has reacted, hot saturated baryta water is added to precipitate all the manganese as $Mn(OH)_2$ and the sulphate as $BaSO_4$, which are filtered and washed with hot water; the slight excess of baryta in the filtrate is precipitated by carbon dioxide, and the filtrate is evaporated to give colourless monoclinic crystals of **barium dithionate**, $BaS_2O_6,2H_2O$.

With a suspension of ferric hydroxide a brownish-red solution of *ferric* sulphite is formed, which passes into a pale green solution of *ferrous* dithionate and sulphite:

$$2Fe(OH)_3 + 3H_2SO_3 = Fe_2(SO_3)_3 + 6H_2O$$
$$Fe_2(SO_3)_3 = FeS_2O_6 + FeSO_3.$$

Cobaltic hydroxide reacts similarly (Carpenter, *J.C.S.*, 1902, **81**, 1) and the reaction with manganese dioxide may be (Meyer, *Ber.*, 1901, **34**, 3406; 1902, **35**, 3429):

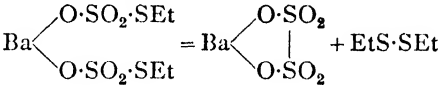
$$2MnO_2 + 3H_2SO_3 = Mn_2(SO_3)_3 + 3H_2O + O$$
$$Mn_2(SO_3)_3 = MnS_2O_6 + MnSO_3$$
$$MnSO_3 + O = MnSO_4.$$

Dithionic acid is obtained by an oxidation reaction and, unlike the other thionic acids, it is oxidised only with difficulty; boiling concentrated hydrochloric acid and potassium bromate slowly oxidise it to sulphate (Anderson,

J. Phys. Chem., 1932, **36**, 2829). Dithionates, unlike salts of higher thionic acids, are not decomposed by sulphides and sulphites. They are all soluble and mostly crystallise with water: no acid salts are known. They may be made by decomposing barium dithionate solution with the metal sulphate or carbonate, filtering from barium sulphate or carbonate, and crystallising. $Na_2S_2O_6$, $K_2S_2O_6$, $CuS_2O_6,4H_2O$, $Ag_2S_2O_6,2H_2O$, $CaS_2O_6,4H_2O$, $MgS_2O_6,6H_2O$, $ZnS_2O_6,6H_2O$, $Al_2(S_2O_6)_3,18H_2O$, $PbS_2O_6,4H_2O$ and $Cr_2(S_2O_6)_3,18H_2O$ are known. A solution of *dithionic acid* is prepared by precipitating barium dithionate solution with dilute sulphuric acid and concentrating on a water bath and then in vacuum over sulphuric acid: above a s. g. of 1·347 it decomposes (Yost and Pomeroy, *J.A.C.S.*, 1927, **49**, 703): $H_2S_2O_6 = H_2SO_4 + SO_2$. The salts decompose similarly on heating: $K_2S_2O_6 = K_2SO_4 + SO_2$.

By the action of sodium amalgam on dithionate solution a sulphite is formed: $S_2O_6'' + 2Na = 2SO_3'' + 2Na^{\cdot}$.

Barium ethyl thiosulphate, formed on adding barium chloride to sodium ethyl thiosulphate solution, rapidly forms barium dithionate and ethyl sulphide (Ramsay, *J.C.S.*, 1875, **28**, 687):



Trithionic acid $H_2S_3O_6$ was discovered by Langlois (1842), who obtained potassium trithionate by warming a saturated solution of potassium hydrogen sulphite with powdered sulphur for three or four days:

$$6KHSO_3 + 2S = 2K_2S_3O_6 + K_2S_2O_3 + 3H_2O.$$

The best method of preparation (Plessy, 1844; Hertlein, *Z. phys. Chem.*, 1896, **19**, 287) is to pass sulphur dioxide into a saturated solution of potassium thiosulphate until a yellow colour develops, allow to stand till colourless, and repeat until no colour forms. On standing the salt crystallises. The reaction, usually formulated: $2K_2S_2O_3 + 3SO_2 = 2K_2S_3O_6 + S$, is more complex, less sulphur separates and some tetra- and pentathionate are formed. A trithionate is formed by oxidising ice-cold saturated sodium thiosulphate solution with hydrogen peroxide:

$$2Na_2S_2O_3 + 4H_2O_2 = Na_2S_3O_6 + Na_2SO_4 + 4H_2O.$$

A solution of *trithionic acid*, prepared by precipitating a concentrated solution of $K_2S_3O_6$ with tartaric, perchloric or hydrofluosilicic acid, decomposes easily on concentration: $H_2S_3O_6 = H_2SO_4 + SO_2 + S$, and the salts also decompose on heating: $K_2S_3O_6 = K_2SO_4 + SO_2 + S$.

Trithionates, except the silver, mercurous and mercuric salts, are soluble: $Na_2S_3O_6,3H_2O$, $K_2S_3O_6$, $Rb_2S_3O_6$, $Cs_2S_3O_6,H_2O$, $BaS_3O_6,2H_2O$, PbS_3O_6. The cupric salt is stabilised by ethylenediamine $[Cu\ en_2]S_3O_6$.

Sodium amalgam forms sulphite and thiosulphate: $S_3O_6'' + 2Na = SO_3'' + S_2O_3'' + 2Na^{\cdot}$, and alkali sulphide forms thiosulphate: $S_3O_6'' + S'' = 2S_2O_3''$. A sulphite does *not* react with a trithionate, but removes sulphur

from a pentathionate and from a tetrathionate, forming a tetrathionate and trithionate, respectively, and a thiosulphate :

$$S_5O_6'' + SO_3'' = S_4O_6'' + S_2O_3'' \text{ (rapid)}$$
$$S_4O_6'' + SO_3'' = S_3O_6'' + S_2O_3'' \text{ (slow).}$$

Tetrathionic acid $H_2S_4O_6$ was discovered by Fordos and Gélis in 1843. The sodium salt is formed in the iodine-thiosulphate titration :

$$2Na_2S_2O_3 + I_2 = Na_2S_4O_6 + 2NaI.$$

EXPT. 14.—To obtain the pure salt a saturated solution of sodium thiosulphate is added drop by drop to a cooled solution of iodine in alcohol, shaking after each addition, until only a pale yellow colour remains. The tetrathionate separates in crystals (sometimes first as an oily concentrated solution) and is washed with alcohol, dissolved in water, reprecipitated with alcohol and dried over sulphuric acid. In solution it slowly decomposes : $Na_2S_4O_6 = Na_2SO_4 + SO_2 + 2S$, and the reaction is accelerated by sodium thiosulphate.

The tetrathionate is formed by *oxidation* of two thiosulphate ions, two electrons being removed : $2S_2O_3'' = S_4O_6'' + 2e$. The reaction is quantitative with iodine, but with other mild oxidising agents some sulphate is also formed :

$$2S_2O_3'' + I_2 = S_4O_6'' + 2I'$$
$$2S_2O_3'' + 2Fe''' = S_4O_6'' + 2Fe''$$
$$2S_2O_3'' + 2Cu'' = S_4O_6'' + 2Cu'$$
$$2S_2O_3'' + H_2O_2 = S_4O_6'' + 2OH'.$$

EXPT. 15.—Add ferric chloride to sodium thiosulphate solution. A deep purple colour due to the ion $Fe(S_2O_3)_2'$ rapidly disappears and a colourless solution free from ferric ions (no colour with KCNS) is formed :

$$2S_2O_3'' + Fe''' = Fe(S_2O_3)_2'$$
$$Fe(S_2O_3)_2' + Fe''' = S_4O_6'' + 2Fe''.$$

Tetrathionate produced in electrolytic oxidation of thiosulphate solution is probably formed by the action of hydrogen peroxide at the anode (Glasstone and Hickling, *J.C.S.*, 1932, 2345, 2800 ; 1933, 829).

With tetrathionate solution sodium amalgam forms thiosulphate : $S_4O_6'' + 2Na = 2S_2O_3'' + 2Na$ (reverse of formation of S_4O_6'' from $2S_2O_3''$), sulphides form thiosulphate and sulphur : $S_4O_6'' + S'' = 2S_2O_3'' + S$, and sulphites slowly form trithionate : $S_4O_6'' + SO_3'' = S_3O_6'' + S_2O_3''$.

The tetrathionates are soluble : $Na_2S_4O_6$, $K_2S_4O_6$, $[Cu\ en_2]S_4O_6$, BaS_4O_6, $2H_2O$, $Zn(HS_4O_6)_2$, PbS_4O_6, $Mn(HS_4O_6)_2$.

Lead acetate and sodium thiosulphate solution precipitate white lead thiosulphate. A suspension of this reacts with iodine to form a solution of lead tetrathionate : $2PbS_2O_3 + I_2 = PbI_2 + PbS_4O_6$, which when filtered and precipitated with dilute sulphuric acid gives a solution of tetrathionic acid. This is fairly stable and can be concentrated on a water bath and in vacuum over sulphuric acid up to a point, but then decomposes : $H_2S_4O_6 = H_2SO_4 + SO_2 + 2S$. The tetrathionates decompose on heating : $K_2S_4O_6 = K_2SO_4 + SO_2 + 2S$.

Pentathionic acid $H_2S_5O_6$, discovered by Wackenroder in 1845, is formed by the interaction of hydrogen sulphide and sulphurous acid in solution, sulphur and tetrathionic acid being also formed. It is possible that the oxide SO is an intermediate product :

$$H_2S + 2SO_2 = 3SO + H_2O$$
$$5SO + H_2O = H_2S_5O_6,$$

the S_5O_6'' ions being partly reduced to S_4O_6'' by SO_3'' ions.

Pentathionic acid (the existence of which was doubted) was studied by Debus in a masterly research on the thionic acids (*J.C.S.*, 1888, **53**, 278). The salts are not stable unless a little hydrochloric or sulphuric acid is added to the solution.

Hydrogen sulphide is passed slowly for a few hours a day into saturated sulphur dioxide solution till all the SO_2 finally disappears. The milky liquid (*Wackenroder's solution*) contains suspended and colloidal sulphur, pentathionic and tetrathionic acids. These are decomposed by alkali, so that only one-third of the amount of KOH required for neutralisation is run into the liquid in a thin stream with constant stirring. Potassium acetate or bicarbonate may be used instead. On spontaneous evaporation, $K_2S_4O_6$ (monoclinic) and $K_2S_5O_6,1\frac{1}{2}H_2O$ (rhombic) crystals form, and may be separated by hand-picking, or (when well-formed) by flotation in a mixture of bromoform and xylene of *d.* 2·2, when $K_2S_4O_6$ sinks and $K_2S_5O_6,1\frac{1}{2}H_2O$ floats. The pentathionate may be recrystallised from warm water acidified with sulphuric acid.

Pentathionate is formed by the action of concentrated hydrochloric acid on concentrated sodium thiosulphate solution containing a little sodium arsenite and cooled at $-10°$ (Raschig, *Schwefel- und Stickstoffstudien*, 1924, 275) : $S_2O_3'' + 2H^{\cdot} = 2SO + H_2O$; $5SO + H_2O = H_2S_5O_6$. The filtered liquid deposits crystals of $Na_2S_5O_6$ and the filtrate contains $H_2S_5O_6$, giving crystals of $K_2S_5O_6,1\frac{1}{2}H_2O$ on adding potassium acetate.

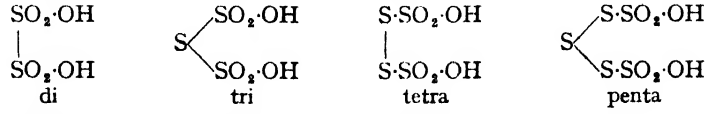
A solution of pentathionic acid is prepared by precipitating a solution of the potassium salt with tartaric acid ; it may be concentrated on a water bath to *d.* 1·3 and in a vacuum desiccator to *d.* 1·6, but then decomposes : $H_2S_5O_6 = H_2SO_4 + SO_2 + 3S$. The salts, which are soluble, decompose on heating : $K_2S_5O_6 = K_2SO_4 + SO_2 + 3S$.

Potassium amalgam reduces pentathionate to tetrathionate and finally to thiosulphate : $S_5O_6'' + 2K = S_4O_6'' + 2K^{\cdot} + S''$, and $S_4O_6'' + 2K = 2S_2O_3'' + 2K^{\cdot}$; sulphide forms thiosulphate and sulphur : $S_5O_6'' + S'' = 2S_2O_3'' + 2S$; and sulphite forms tetrathionate and thiosulphate : $S_5O_6'' + SO_3'' \rightleftharpoons S_4O_6'' + S_2O_3''$.

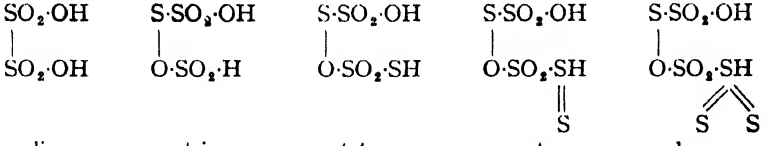
Hexathionic acid $H_2S_6O_6$, according to Debus, is contained in Wackenroder's solution, from which, after separation of $K_2S_4O_6$ and $K_2S_5O_6$, he obtained warty crusts of $K_2S_6O_6$. The potassium salt is prepared (Weitz and Achterberg, 1928 ; Partington and Tipler, *J.C S.*, 1929, 1382) by adding a solution of 1 mol of potassium nitrite and 3 mols of potassium thiosulphate to well-cooled hydrochloric acid in a large flask, with vigorous shaking, the oxides of nitrogen being removed by a current of air, and the solution cooled in a freezing mixture. Potas-

sium chloride separates and is removed. On concentrating the solution under reduced pressure, potassium hexathionate crystallises.

Structures of the thionic acids.—Several sets of formulae have been proposed for the thionic acids. Blomstrand (1869) and Mendeléeff (1870) suggested that $-SO_3OH$ groups are linked by sulphur atoms :

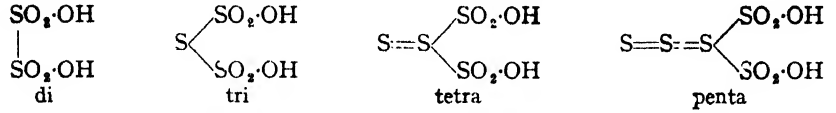


Debus (1888) considered that the central linking group was —S—O— :

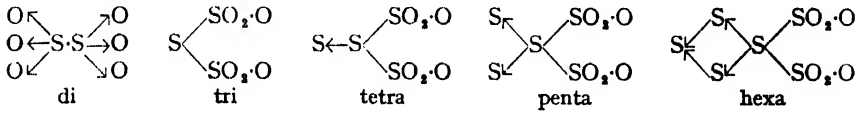


Hertlein (1896) found that polythionates of mercury and silver do not form complex compounds, and from this and the molecular refractions of the salts he concluded that the metal is attached to oxygen as in Blomstrand's and Mendeléeff's formulae, rather than to sulphur as in Debus's formulae, since these metals in combination with sulphur readily form complex compounds.

Vogel (*J.C.S.*, 1925, **127**, 2248) proposed the formulae :



which are similar to those now adopted (Hägg, 1932 ; Huggins and Frank, 1928–33 ; Zachariasen, 1932–4), those for di- and tri-thionates being based on X-ray evidence ; the ions are :



The dithionate ion is a trigonal bipyramid, and the —S— angle in the trithionate ion is about 103°.

Although dithionic acid does not form acid salts, the conductivities of the sodium salt, and Ostwald's rule (p. 149), show that it is dibasic, $H_2S_2O_6$ and not HSO_3.

CHAPTER XXV

SELENIUM AND TELLURIUM

Selenium

SELENIUM was discovered by Berzelius in 1817 in a deposit in a lead chamber making sulphuric acid. The name is from the Greek *selene*, the moon, on account of the analogy of the element with tellurium, named from the Latin *tellus*, the earth. Many important compounds of selenium were discovered by Berzelius; selenic acid was discovered by Mitscherlich in 1827.

Selenium is intermediate between sulphur and tellurium in its properties.

Selenium occurs native in Mexico and California, and in some native sulphur, particularly Japanese, and metallic selenides of lead PbSe, copper Cu_2Se and silver Ag_2Se occur at Clausthal (Harz), mercury selenide HgSe in Mexico, and the important ore *zorgite*, a double selenide of copper and lead with some iron and silver and as much as 31 p.c. of Se, in the Argentine. *Crookesite* $(Cu,Tl,Ag)_2Se$ is found at Skrikerum in Sweden. Many kinds of pyrites contain selenium, which finds its way into the flue dusts and chamber deposits of sulphuric acid works and into the commercial acid. In making sodium sulphate with this acid (p. 314) the selenium passes as chloride into the hydrochloric acid.

Selenium occurs in soil of the arid plains of Dakota, Wyoming and Kansas, making the herbage poisonous to animals, and it may pass into wheat (Godden, *J.S.C.I.*, 1939, **58**, 791; Painter, *Chem. Rev.*, 1941, **28**, 179). Most vegetables, especially spinach, and bones and teeth, contain it in traces.

Selenium may be extracted from vitriol chamber deposits, etc., by digesting with fuming sulphuric acid: $Se + 2SO_3 = SeO_2 + 2SO_2$, or with potassium cyanide solution when it dissolves as **potassium selenocyanate**: $KCN + Se = KCNSe$, and on adding hydrochloric acid selenium is precipitated as a red powder: $KCNSe + HCl = KCl + HCN + Se$. It is purified by distillation or by evaporating to dryness with nitric acid, when solid **selenium dioxide** SeO_2 is formed, which can be sublimed, or recrystallised as **selenious acid** H_2SeO_3, a solution of which is reduced by sulphur dioxide: $H_2SeO_3 + 2SO_2 + H_2O = Se + 2H_2SO_4$.

Selenium is extracted from the anode slimes of electrolytic copper refining which may contain as much as 96 p.c. together with tellurium, although 1 to 18 p.c. Se and 0·25 to 2·5 p.c. Te are usual.

In extracting selenium and tellurium from anode slimes these may be roasted, when SeO_2 and some TeO_2 sublime, or fused with sodium nitrate and sand, when selenite and tellurite are formed and are extracted with water. Sulphuric acid precipitates TeO_2 (which is reduced by heating with carbon) and sulphur dioxide precipitates selenium, which is purified by distilling in steel retorts.

Selenium is used in making red glass, enamels and glazes, and the red pigment cadmium selenide (p. 392), and in photoelectric cells (p. 337); its compounds are used in photographic toning and selenobenzamide in froth flotation. Selenium has been used in vulcanising rubber; in conjunction with sulphur it prevents surface crystallisation or "bloom."

Like sulphur, selenium exists in several *allotropic modifications* (Saunders, *J. Phys. Chem.*, 1900, **4**, 423; Briegleb, *Z. phys. Chem.*, 1929, **144**, 321):

1. **Amorphous selenium.** (*a*) *Vitreous selenium*, an opaque almost black lustrous solid, s. g. 4·28, giving a red powder, and formed by suddenly cooling melted selenium. It softens at 50° and if rapidly heated to 220° is liquid but viscous. Above 60°–80° it changes fairly quickly into *metallic selenium* (no. 3). (*b*) *Red amorphous selenium*, a dark red powder, s. g. 4·26, precipitated from a solution of selenious acid by sulphur dioxide, or by hydrochloric acid from a solution of KCNSe, or formed (as "flowers of selenium") by subliming selenium in a sealed tube. Amorphous selenium is slightly soluble in carbon disulphide (about 0·1 p.c. at the b.p.) and readily in selenium oxychloride. (*c*) *Colloidal selenium* formed as a red sol by mixing dilute solutions of selenious and sulphurous acids, or by the action of hydrazine hydrate on SeO_2 and dilution.

2. **Monoclinic selenium**, obtained in red crystals by letting forms 1*a* or 1*b* stand in contact with carbon disulphide, by adding benzene to a solution of selenium in carbon disulphide, or by the spontaneous evaporation of this solution. Two stable crystalline varieties are known, s. g. 4·47 (cf. sulphur). If heated rapidly the red crystals fuse at 200° with partial conversion into metallic selenium and the metastable melting point is probably 170°–180° (cf. α-sulphur).

3. **Metallic selenium** formed, with evolution of heat, when any other variety is heated at 200°–220° for some time, is silvery-grey, s. g. 4·80, gives a black powder (red if very fine), and is insoluble in carbon disulphide (about 1 p.c. of soluble selenium is always present) but soluble in chloroform. It has been obtained by sublimation in hexagonal crystals isomorphous with tellurium.

Briegleb (1929) from X-ray examination concluded that vitreous selenium is amorphous, monoclinic selenium consists mostly of Se_2 molecules, and metallic selenium mostly of Se molecules. This is doubtful, as the transformation of Se_2 to Se would then be exothermic.

Selenium boils at 684·8° giving a dark red vapour, the density of which falls with rise of temperature; at lower temperatures Se_8 and Se_6 molecules seem to be present, above 1400° Se_2 molecules only. The molecular weight in solution in phosphorus corresponds with Se_8.

The electrical conductivity of metallic selenium is very small in the dark, but on exposure to light it increases rapidly, the original conductivity being recovered (with a time-lag) in the dark (Willoughby Smith, 1873). The conductivity varies as the square root of the intensity of the light. This property, which is probably due to an inner photoelectric effect (liberation of electrons in the surface layer of the solid) is utilised in photoelectric cells.

Selenium combines with many metals to form *selenides* and alkali metal selenides and polyselenides, Na_2Se, Na_2Se_2, Na_2Se_3, Na_2Se_4 and Na_2Se_5, analogous to the sulphides (p. 313), are formed. It reduces hot silver nitrate solution: $3Se + 4AgNO_3 + 3H_2O = 2Ag_2Se + H_2SeO_3 + 4HNO_3$.

Hydrogen selenide H_2Se is formed in small amounts on heating selenium in hydrogen: $H_2 + Se \rightleftharpoons H_2Se$, although most of the selenium sublimes in glittering crystals (Robinson and Scott, *J.C.S.*, 1932, 1972), and by the action of nascent hydrogen on selenious acid (Meunier, 1916). On heating iron filings with selenium ferrous selenide is formed, which gives H_2Se with acids: $FeSe + 2HCl = FeCl_2 + H_2Se$. Pure H_2Se is obtained by the action of water on aluminium selenide: $Al_2Se_3 + 6H_2O = 2Al(OH)_3 + 3H_2Se$. Hydrogen selenide is a colourless inflammable gas with a very offensive smell and strong action on the mucous membranes and is poisonous. It is less stable than hydrogen sulphide. It is soluble in water to a feebly acid solution which precipitates selenides of many metals, and oxidises on exposure to air, selenium being precipitated. It combines with ammonia gas to form solid $(NH_4)_2Se$. The normal density of the gas is 3·6696 g./lit., corresponding with a molecular weight 82, and it leaves its own volume of hydrogen when decomposed by heated tin, hence the formula is H_2Se. The b.p. is $-41·7°$ and the m.p. $-64°$.

Halogen Compounds of Selenium

SeF_6 colourless gas, m.p. $-39°$, b.p. $-34·5°$.
SeF_4 colourless liq., m.p. $-13·2°$, b.p. 93°.
Se_2Cl_2, brown-red liq., s. g. 2·9, m.p. $-85°$, b.p. 130° (d.).
$SeCl_4$ yellowish-white solid, cubic, subl. 180°, m.p. 305°.
Se_2Br_2 dark-red liq., s. g. 3·6, m.p. $-46°$, b.p. 227° (d.), 54°/0·18 mm.
$SeBr_4$ orange-red solid, m.p. 75° (d.).
$SeOF_2$ colourless liq., s. g. 2·67, m.p. 4·6°, b.p. 124°.
$SeOCl_2$ pale yellow liq., s. g. 2·42 (22°), m.p. 8·5°, b.p. 176·4° (d.).
$SeOBr_2$ reddish-yellow solid, m.p. 41·6°, b.p. 217° (d.).

The reddish-brown liquid **selenium monochloride** Se_2Cl_2 is formed by passing chlorine over selenium. It decomposes on heating, giving the more stable tetrachloride: $2Se_2Cl_2 = 3Se + SeCl_4$, and is slowly decomposed by water: $2Se_2Cl_2 + 3H_2O = H_2SeO_3 + 3Se + 4HCl$. The pale yellow solid **tetrachloride** is formed by the action of excess of chlorine on selenium, or by heating selenium dioxide and PCl_5, distilling off the $POCl_3$ in a current of carbon dioxide, and subliming: $SeO_2 + 2PCl_5 = SeCl_4 + 2POCl_3$. It sublimes without fusion and the yellow vapour is dissociated (Simons, *J.A.C.S.*, 1930, **52**, 3483): $2SeCl_4 \rightleftharpoons Se_2Cl_2 + 3Cl_2$. It is decomposed by water: $SeCl_4 + 3H_2O = H_2SeO_3 + 4HCl$.

The reddish-brown liquid **selenium monobromide** Se_2Br_2 is more stable than the orange-red solid **tetrabromide** $SeBr_4$. Both are formed from the elements. The solid acid H_2SeBr_6 and salts are known. No iodides are known.

The liquid **oxyfluoride** $SeOF_2$ is made by passing $SeOCl_2$ vapour over AgF in platinum apparatus at 140°–200° and condensing. It attacks glass readily: $2SeOF_2 + SiO_2 = 2SeO_2 + SiF_4$ (Prideaux and Cox, *J.C.S.*, 1928, 739).

The light yellow liquid **oxychloride** $SeOCl_2$ is formed by the partial hydrolysis of the tetrachloride: $SeCl_4 + H_2O = SeOCl_2 + 2HCl$, and on heating the dioxide and tetrachloride in a sealed tube or suspending them in CCl_4 and distilling off

the solvent: $SeO_2 + SeCl_4 = 2SeOCl_2$. The liquid has a high dielectric constant (46·2). It mixes with many organic liquids and reacts with most metals and oxides; potassium reacts explosively but sodium is unaffected, and whilst niobium and molybdenum are attacked tantalum and tungsten are not. The **oxybromide** $SeOBr_2$ is obtained by distilling $SeOCl_2$ with NaBr, or by mixing together Se, SeO_2 and $2Br_2$ and warming: it is very reactive. The additive compounds $SeO_2,2HCl$, $SeO_2,4HCl$ and $SeO_2,4HBr$ are formed.

Oxides and Oxyacids of Selenium

SeO_2 tetragonal crystals, s. g. 3·95, m.p. 345°, subl. 315°.

SeO_3 solid.

H_2SeO_3 hexagonal crystals, s. g. 3·0, loses water on heating.

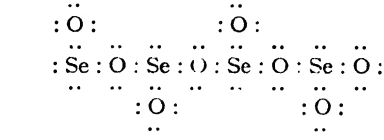
H_2SeO_4 hexagonal prisms, s. g. 2·95, m.p. 58°, b.p. 265° (d.); H_2SeO_4,H_2O, m.p. 25·5°; $H_2SeO_4,4H_2O$, m.p. −51·7°.

All are colourless or white.

The unpleasant smell of rotten horse-radish noticed when selenium burns in air has been ascribed to a gaseous monoxide SeO, which has not been isolated; it may be due to hydrogen selenide.

Selenium burns, but not very easily, when heated in air, and more readily in oxygen, with a blue flame forming the white crystalline volatile **dioxide** SeO_2, very soluble in water.

The crystals of selenium dioxide contain chains of selenium and oxygen atoms:



with an unshared pair of electrons occupying the fourth tetrahedral position of Se; there is some double bond character in the Se—O links. The Se to O distance is 1·73 A. for the unshared and 1·78 A. for the shared oxygens (McCullough, *J.A.C.S.*, 1937, **59**, 789).

SeO_2 forms a yellow liquid and vapour. The vapour density is normal, but in solution in $SeOCl_2$ the molecule is $(SeO_2)_3$.

By evaporating a solution of SeO_2 in water or selenium in hot nitric acid, very soluble hexagonal prisms of **selenious acid** H_2SeO_3 are formed. It gives acid and normal **selenites**, *e.g.* $KHSeO_3$ and K_2SeO_3, and superacid salts, $KH_3(SeO_3)_2$. Heteropolyacids are formed with vanadic, molybdic and uranic acids. $CaSeO_3$ and $BaSeO_3$ are sparingly soluble. Selenious acid and selenites are easily reduced to red selenium, *e.g.* by organic matter in dust.

Selenium trioxide SeO_3 is formed, mixed with some SeO_2, as a white deliquescent solid by passing a glow discharge through a mixture of oxygen and selenium vapour at 4 mm. pressure (Rheinboldt, 1930; Kramer and Meloche, *J.A.C.S.*, 1934, **56**, 1081). The corresponding **selenic acid** H_2SeO_4 is produced by the action of chlorine on selenium or selenious acid suspended in water:

$Se + 4H_2O + 3Cl_2 = H_2SeO_4 + 6HCl$, by the action of bromine on silver selenite in water: $Ag_2SeO_3 + H_2O + Br_2 = 2AgBr + H_2SeO_4$, by oxidising selenious acid in nitric acid with chloric acid, or selenious acid with permanganate, or by electrolytic oxidation. The solution may be evaporated until at 265° it contains 95 p.c. of H_2SeO_4, when it decomposes on further heating. If this liquid is placed over sulphuric acid in a vacuum desiccator until it contains 97·4 p.c. of H_2SeO_4 (s. g. 2·627) and then strongly cooled it forms colourless hexagonal crystals of pure selenic acid, m.p. 58°. It forms crystal hydrates with 1 and $4H_2O$. The acid is very hygroscopic and evolves heat with water; the concentrated acid chars organic matter and dissolves sulphur to a blue liquid. Potassium selenate is formed on fusing selenium with nitre (Mitscherlich, 1827) and sodium selenate on heating selenium with sodium peroxide. (Nitric acid oxidises selenium only to *selenious* acid.)

Selenic acid on heating dissolves copper and gold, forming $CuSeO_4$ and $Au_2(SeO_4)_3$, part of the acid being reduced to selenious acid. The dilute acid dissolves zinc: $Zn + H_2SeO_4 = ZnSeO_4 + H_2$, but iron receives a thin protective coating of selenium and is not dissolved. Calcium selenate forms a hemihydrate $CaSeO_4,\frac{1}{2}H_2O$, like plaster of Paris. Barium selenate is rather more soluble in water (0·08 g. per lit. at 25°) than barium sulphate and occludes salts more easily. Double salts are formed with alkali selenates and selenates of Fe(ous), Cu, Co, etc.

According to Mitscherlich selenic acid is not reduced by hydrogen sulphide or sulphur dioxide, but Benger (*J.A.C.S.*, 1927, **39**, 2171) says it is reduced, with some difficulty. It is reduced to selenious acid by boiling with dilute hydrochloric acid: $H_2SeO_4 + 2HCl = H_2SeO_3 + H_2O + Cl_2$.

White solid **nitrososelenic acid** $SeO_2(OH)O{\cdot}NO$, or $(NO)HSeO_4$, m.p. 80°, is formed from liquid N_2O_3 and ice-cold anhydrous H_2SeO_4 (Meyer and Wagner, 1922). Selenium dissolves in fused sulphur trioxide or fuming sulphuric acid, more easily on warming, to a green solution containing **selenosulphur trioxide** $SSeO_3$ (sulphur gives a blue solution of S_2O_3 and tellurium a red solution of $STeO_3$).

Selenium dissolves in potassium sulphite solution forming **potassium selenothiosulphate** K_2SSeO_3 (analogous to the thiosulphate), which can be obtained in colourless crystals.

Salts of **selenotrithionic acid** $Se(SO_2{\cdot}OH)_2$ are formed by the action of selenium acetylacetone (from acetylacetone and $SeCl_4$) on alkali hydrogen sulphites:

$$(C_5H_6O_2 : Se)_2 + 4KHSO_3 = 2Se(SO_2{\cdot}OK)_2 + 2C_5H_8O_2.$$

A solution of the free acid (which can be concentrated to 50 p.c.) is formed from selenium acetylacetone and sulphurous acid. A salt of **selenopentathionic acid** $H_2SeS_4O_6$ is formed from selenious acid and sodium thiosulphate in weakly acid solution: $SeO_2 + 4Na_2S_2O_3 + 4HCl = 4NaCl + Na_2S_4O_6 + Na_2SeS_4O_6 + 2H_2O$.

An explosive orange-red **selenium nitride** Se_4N_4 (cf. S_4N_4) is precipitated on passing dry ammonia into a dilute solution of $SeOCl_2$ in benzene, or by the action of liquid ammonia on $SeBr_4$ in presence of CS_2 (Strecker and Claus, 1923). **Selenophen** C_4H_4Se (analogous to thiophen) is formed from selenium and acetylene at 400° (Briscoe and Peel, *J.C.S.*, 1928, 1741).

Tellurium

Native tellurium occurs in small amounts and was called by early mineralogists *aurum paradoxum* or *aurum problematicum*, on account of its lustre. J. F. Müller von Reichenstein in 1782 sent a specimen of it to Bergman, who reported that it was a peculiar metal similar to antimony. Klaproth in 1798 examined it and called it tellurium (Latin *tellus*, the earth). Berzelius in 1832, after a thorough investigation characteristic of his work, pointed out its analogies to sulphur and selenium (which he had discovered in 1817).

Tellurium is rather rare. It is found native in Central Europe, Colorado and Bolivia, and with selenium in Japanese sulphur, but usually occurs as tellurides: *sylvanite* or *graphic tellurium* $(Ag,Au)Te_2$, *nagyagite* or *black tellurium* $(Au,Pb)_2(Te,S,Sb)_3$, *hessite* Ag_2Te, and *tetradymite* Bi_2Te_3. Gold tellurides are important for gold extraction in Australia and Colorado.

Tellurium may be extracted from some silver and bismuth ores, or from the anode slimes of copper refining (p. 329). Less than 0·1 p.c. gives lead a greater tensile strength and resistance to acids (Singleton and Jones, *J.S.C.I.*, 1933, **52**, 211 R.) and tellurium has also been proposed for use as a dark finish in electroplating silver, for compounding rubber, and as diethyl telluride as an anti-knock for petrol. It seems, however, to find little use, and its compounds usually have offensive properties.

Bismuth ores are dissolved in hydrochloric acid, tellurium precipitated with sodium sulphite, and purified by boiling with sodium sulphide solution and powdered sulphur, then adding sodium sulphite, when tellurium separates as a greyish-black precipitate, which becomes silver-white on fusion. Ores containing silver telluride, and anode slimes, are treated with fuming sulphuric acid and the diluted solution precipitated with zinc or sulphur dioxide.

Tellurium can be deposited in smooth thick layers on a lead cathode from a solution of TeO_2 in hydrofluoric and sulphuric acids; with a tellurium anode containing selenium, the latter deposits as a slime (Mathers and Turner, 1928).

Tellurium forms hexagonal crystals, is brittle and easily powdered, has a bright lustre like antimony, a fairly high s. g. of 6·31, conducts electricity like a metal, and readily forms an amalgam. An amorphous variety, s. g. 6·015, is precipitated by sulphur dioxide from tellurous or telluric acid. Tellurium melts at 452·5°, and boils at 1390° (478° in a nearly perfect vacuum) forming a golden-yellow vapour. At 671° the vapour pressure is only 15 mm. (Doolan and Partington, *Trans. Faraday Soc.*, 1924, **20**, 342). The vapour density at 1400° is slightly higher than corresponds with Te_2. When heated in air tellurium burns with a blue flame forming white vapours of *tellurium dioxide* TeO_2.

A red colloidal solution obtained by reducing telluric acid with hydrazine behaves towards electrolytes like a metal sol (Doolan, *J. Phys. Chem.*, 1925, **29**, 178).

Tellurium combines with many metals to form *tellurides*, and dark-red alkali polytellurides.

Hydrogen telluride H_2Te, prepared in an impure state by Davy in 1810 from zinc telluride and acid, is obtained pure from aluminium telluride and dilute hydrochloric acid, or by the electrolysis of 50 p.c. sulphuric or phosphoric acid at $-20°$ with a tellurium cathode, and at once drying and liquefying the gas (b.p. $-1·8°$, m.p. $-57°$) (Dennis and Anderson, *J.A.C.S.*, 1914, **36**, 882).

Hydrogen telluride is a colourless gas with an unpleasant smell, less stable than hydrogen selenide but fairly stable in the dark when pure. Exposure to light decomposes it, especially when moist: $H_2Te = H_2 + Te$. An equal volume of hydrogen remains after heating with zinc, and this result, with the gas density, gives the formula H_2Te. The gas burns in air with a pale blue flame: $2H_2Te + 3O_2 = 2H_2O + 2TeO_2$. The solution oxidises in air and becomes red, from separation of tellurium.

Hydrogen telluride is a fairly strong acid and hydrogen selenide is stronger than hydrogen sulphide: the p.c. ionisations in $0·1N$ solutions are: H_2S 0·1, H_2Se 4·1, H_2Te 50. The acidic character thus increases with atomic weight in the group O to Te.

Halogen Compounds of Tellerium

TeF_6 colourless gas, m.p. $-36°$, subl. $-35·5°$.
$TeCl_2$ black solid, m.p. 175°, b.p. 324°.
$TeCl_4$ white solid, m.p. 224°, b.p. 390°.
$TeBr_2$ black solid, m.p. 210°, b.p. 339°.
$TeBr_4$ orange-red solid, m.p. 380°, b.p. 421°.
TeI_4 grey-black solid, m.p. 259°.

Tellurium combines with fluorine with incandescence to form a gaseous **hexafluoride** TeF_6 (Prideaux, *J.C.S.*, 1906, **89**, 316), and an **oxyfluoride**, $TeOF_2,\frac{1}{2}H_2O$, is formed in white crystals by the action of anhydrous hydrofluoric acid on TeO_2 (Prideaux and Millott, *J.C.S.*, 1926, 520). The hexafluoride is only slowly hydrolysed by water: $TeF_6 + 6H_2O = 6HF + H_6TeO_6$ (telluric acid). Excess of chlorine forms with tellurium the stable white crystalline **tetrachloride** $TeCl_4$, very hygroscopic and hydrolysed by water: $TeCl_4 + 2H_2O = TeO_2 + 4HCl$. The vapour is stable at 530°. On heating $TeCl_4$ with tellurium the black solid **dichloride** $TeCl_2$ is formed. $TeCl_4$ and hydrochloric acid form H_2TeCl_6, salts of which (*e.g.* K_2TeCl_6) are isomorphous with corresponding stannic, plumbic and platinic compounds and with K_2SiF_6 (Simons, *J.A.C.S.*, 1930, **52**, 3488).

Tellurium forms a **dibromide** $TeBr_2$ and **tetrabromide** $TeBr_4$, and (unlike sulphur and selenium) a **tetraiodide** TeI_4, formed from the elements in iron-grey crystals, and also in solution by the reaction $TeO_2 + 4HI = TeI_4 + 2H_2O$.

Oxides and Oxyacids of Tellurium

Tellurium forms the oxides TeO, TeO_2 and TeO_3; tellurous acid is known as salts, the tellurites, *e.g.* K_2TeO_3; ordinary telluric acid is H_6TeO_6.

Black tellurium monoxide TeO is formed by heating $STeO_3$ (see below) in vacuum at 230°: $STeO_3 = TeO + SO_2$ (Divers and Shimose, 1883; Doolan and Partington,

J.C.S., 1924, **125**, 1402). With concentrated sulphuric acid it forms white crystals of tellurium sulphate $Te(SO_4)_2$: $2TeO + 3H_2SO_4 = Te(SO_4)_2 + STeO_3 + 3H_2O$.

The white solid (tetragonal) **tellurium dioxide** TeO_2, formed by burning tellurium in air or oxygen, or by evaporation with nitric acid and heating the basic nitrate $2TeO_2,HNO_3$, is only sparingly soluble and has no acid reaction. It dissolves in alkalis forming *tellurites*, *e.g.* K_2TeO_3, from which acids precipitate a hydrated form called *tellurous acid*, which reddens litmus. Tellurites are also formed by fusing TeO_2 with alkalis or alkali carbonates. The formation of the *basic nitrate* $2TeO_2,HNO_3$ or $Te_2O_3(OH)NO_3$ (rhombic crystals) by evaporating tellurium or the dioxide with nitric acid shows that TeO_2 is amphoteric.

Tellurium trioxide TeO_3 is an orange-yellow powder formed on heating telluric acid. It decomposes when strongly heated: $2TeO_3 = 2TeO_2 + O_2$. It is insoluble in water, but telluric acid is formed in other ways.

Telluric acid is best prepared by dissolving tellurium powder in aqua regia, adding chloric acid in small portions, evaporating in vacuum, precipitating with nitric acid, and recrystallising from water. It forms white crystals of the composition H_6TeO_6, in two crystalline forms, cubic and monoclinic. Telluric acid is sparingly soluble in cold but readily in hot water. It is a weak acid.

The molecular weight in solution corresponds with H_6TeO_6, and thin plates of the crystals, unlike true hydrates (*e.g.* $CuSO_4,5H_2O$) are not permeated by water vapour. The methyl ester $Te(OCH_3)_6$ and silver salt Ag_6TeO_6 are known, hence the acid is H_6TeO_6 and not $H_2TeO_4,2H_2O$. The X-rays show that the TeO_6 radical is octahedral (Pauling, *J.A.C.S.*, 1935, **91**, 367). Below 10° the solution of telluric acid deposits the hydrate $H_2TeO_4,6H_2O$.

On heating H_6TeO_6 in a sealed tube at 140° it forms *allotelluric acid* $(H_2TeO_4)_x$, a fairly strong acid (Mylius, 1901; Patry, *Bull. Soc. Chim.*, 1936, **3**, 845). At 100°–220° H_6TeO_6 loses water and forms a white powder of *metatelluric acid* $(H_2TeO_4)_n$.

The **tellurates** are formed by fusing tellurites with potassium nitrate or passing chlorine into alkaline solutions of tellurites:

$$K_2TeO_3 + 2KOH + Cl_2 = K_2TeO_4 + 2KCl + H_2O.$$

They are *not* isomorphous with sulphates or selenates. Some tellurates exist in two forms, a colourless salt soluble in water and acids and a yellow insoluble form. Normal, acid, and superacid salts are known:

$$K_2TeO_4,5H_2O, \quad K_2Te_2O_7,4H_2O, \quad K_2Te_4O_{13},4H_2O$$

(cf. chromates and polychromates). Tellurates are reduced to tellurites by boiling hydrochloric acid: $K_2TeO_4 + 2HCl = K_2TeO_3 + Cl_2 + H_2O$, and (unlike selenates) are easily reduced to tellurium by sulphur dioxide. Barium tellurate $BaTeO_4,3H_2O$ is fairly soluble in water.

Tellurium dissolves in warm concentrated (especially in fuming) sulphuric acid to a cherry-red solution and from tellurium and sulphur trioxide the red solid $STeO_3$ (analogous to the blue S_2O_3 and green $SSeO_3$) is formed. When fused with potassium cyanide tellurium does not form a compound analogous to KCNS or KCNSe but only the telluride K_2Te.

The atomic weight of tellurium.—The atomic weights of tellurium (127·60) and iodine (126·92) are in the reverse of the order expected from the positions in the periodic table, and it was suspected that tellurium might contain an unknown element of higher atomic weight. Attempts by Brauner (*J.C.S.*, 1889, **55**, 382) to separate this were unsuccessful.

H. B. Baker and A. H. Bennett (*J.C.S.*, 1907, **91**, 1849) determined the atomic weight in various ways with tellurium from different sources, finding the same result in all cases. They tried to separate the tellurium by: (1) fractional crystallisation of telluric acid, (2) boiling barium tellurate with water (the solubility increases in the series $BaSO_4 \rightarrow BaSeO_4 \rightarrow BaTeO_4$), (3) fractional distillation of Te, $Te(C_2H_5)_2$, $TeCl_4$, and TeO_2, (4) fractional electrolysis of tellurium compounds, (5) fractional precipitation of $TeCl_4$ with water. The results were all negative. By heating TeO_2 with sulphur in a small tube (Fig. 305) the reaction $TeO_2 + S = Te + SO_2$ occurred, the excess of sulphur being kept back with silver foil. By this method (which had been used by Berzelius in 1834), and the synthesis of $TeBr_4$, the value Te = 127·60 was obtained, which is higher than the atomic weight of iodine, I = 126·92. Flint (1909) claimed to have separated fractions from tellurium by method (5), but his work was not substantiated by Harcourt and Baker (*J.C.S.*, 1911, **99**, 311).

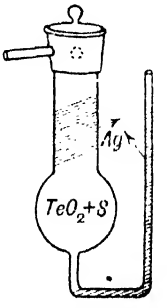


FIG. 305.—Atomic weight of tellurium.

Although Aston's mass spectrograph results seemed to indicate that the chemical atomic weight was seriously in error, Hönigschmid (1933) fully confirmed Baker and Bennett's result, finding Te = 127·59 from the ratio $4Ag : TeBr_4$, and Bainbridge (*Phys. Rev.*, 1932, **39**, 1021) showed that earlier workers had missed several isotopes of tellurium, the average atomic weight from the mass spectrograph method being 127·58. Iodine, on the other hand, is a simple element.

CHAPTER XXVI

METALS OF GROUP SIX

Chromium

A RED Siberian mineral now called *crocoisite* described by J. G. Lehmann in 1766 was found by Vauquelin and by Klaproth in 1797 to be lead chromate ($PbCrO_4$). The name chromium (Greek *chroma*, colour) refers to the large number of coloured compounds formed by the element. Impure metallic chromium was obtained by Vauquelin by reducing the green oxide Cr_2O_3 with carbon at a white heat.

Chromium occurs in small amounts in some iron meteorites. The commonest ore is *chromite* or *chrome ironstone*, ferrous chromite $FeCr_2O_4$ or FeO,Cr_2O_3, a spinel (p. 422), s. g. 4·4. Rarer minerals are *chrome ochre* Cr_2O_3, and *chromitite* $Fe_2O_3,2Cr_2O_3$.

Chromite is mined in Rhodesia, the Transvaal, Cuba, Greece, Turkey, India, Russia, Yugoslavia, the Philippines and New Caledonia. It is very refractory and is made into chrome bricks for furnace linings or to separate silica bricks from magnesia bricks in basic hearth steel furnaces. From chromite either iron-chromium alloys (p. 739) or dichromates (p. 748) are made technically.

Metallic chromium is formed by passing sodium vapour over red-hot chromic chloride (Fremy, 1857): $CrCl_3 + 3Na = Cr + 3NaCl$, or by heating Cr_2O_3 in very dry hydrogen at 1500°, or with carbon in the electric furnace and reheating with more Cr_2O_3 or quicklime to remove carbon (Moissan, 1893). The simplest preparation is by the aluminothermic reduction of Cr_2O_3 with aluminium (Goldschmidt, *J.S.C.I.*, 1898, **17**, 543, 584): $Cr_2O_3 + 2Al = 2Cr + Al_2O_3$. The chromium forms a fused mass of 99·5 p.c. purity. It contains a little iron and silicon.

A mixture of oxide and aluminium powder is ignited in a crucible by a small cartridge of 15 pts. of barium peroxide and 2 pts. of magnesium powder placed in a depression in the mixture and kindled by a small piece of burning magnesium ribbon. The "thermit" reaction evolves so much heat that the alumina fuses and crystallises on cooling.

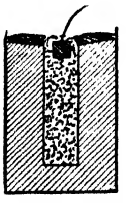


FIG. 306.—Thermit reaction.

A tin canister 10 in. by 6 in. is filled with coarsely-powdered fluorspar and a depression 2 in. × 8 in. made by a large test-tube. The mixture of oxide and aluminium powder is pressed into this, and the igniter placed on the top (Fig. 306). The fluorspar is a good heat insulator. A mixture of aluminium powder with an equal or double weight of calcium turnings is more active than aluminium alone, and is used in the case of difficultly reducible oxides such as Cr_2O_3, or a mixture of 4 pts. Cr_2O_3, 1 of powdered fused $K_2Cr_2O_7$ and 1·9 of Al powder.

Pure chromium is obtained by electrolysing a solution of chromic chloride $CrCl_3$ with a mercury cathode and heating the amalgam in vacuum to remove mercury, or in compact ductile form by heating chromic chloride with calcium turnings in a nickel-steel bomb (Kroll, 1935). It was obtained by Bunsen in 1854 by electrolysis of a solution of chromous chloride $CrCl_2$ containing a little chromic chloride. Chromium is now deposited electrolytically from a solution of 250 g. of CrO_3 and 2·5 g. of H_2SO_4 per lit. with a lead anode covered with electrodeposited lead dioxide. A high current density (150 amp. per sq. ft.) is used. Chromium plating is very bright and hard and (unlike nickel plating) is not attacked by sulphur compounds in the atmosphere. In plating iron a thin film of copper or nickel is first deposited, as this prevents peeling of the chromium.

Chromium is malleable, silver-white with a bluish tinge, s. g. 7·14, m.p. 1800°. It has a high b.p. (2200°) but distils in the electric furnace, depositing in crystals. The *pure* metal is not very hard, the hardness of the electrodeposited metal (9 Mohs) is due to the crystal form and to occluded hydrogen (up to 250 vols.). There are three crystalline forms: α, body-centred cubic (like W); β, hexagonal close-packed (like Mg); and γ, a body-centred cubic lattice with 58 atoms in the unit cell. Chromium burns brilliantly in the oxyhydrogen flame to Cr_2O_3 and decomposes steam at a red heat: $2Cr + 3H_2O = Cr_2O_3 + 3H_2$. The finely divided metal left on heating the amalgam is pyrophoric and combines with atmospheric oxygen and nitrogen. The compact metal dissolves slowly in dilute sulphuric and hydrochloric acids, more rapidly on heating, forming blue solutions of *chromous salts* containing $Cr^{\cdot\cdot}$, *e.g.* $Cr + 2HCl = CrCl_2 + H_2$. The solutions rapidly absorb atmospheric oxygen, forming green solutions of *chromic salts*: $4CrCl_2 + 4HCl + O_2 = 4CrCl_3 + 2H_2O$.

Hot concentrated sulphuric acid attacks chromium rapidly, with evolution of sulphur dioxide. Dilute nitric acid does not dissolve the pure metal, and in concentrated nitric acid the metal becomes passive and is then not attacked by dilute acids. The passivity is due to an oxide film and is also induced by exposure to air or dipping into chromic acid. The passivity is removed by touching the metal in dilute sulphuric acid with zinc.

Some specimens of chromium, but not the pure metal, show a *periodic* rate of solution in acids; this is due to a catalyst, either a foreign metal or a colloid present in small quantities (Hedges and Myers, *J.C.S.*, 1924, **125**, 604).

The alloy *ferrochrome* of 60–70 p.c. chromium with iron, made by reducing chrome ironstone with carbon in the electric furnace, is used in making *chrome steel*. It is not attacked by acids. An alloy of chromium, nickel and iron is used for armour-plate. *Stainless steel* is ordinary steel with 12–14 p.c. of chromium and up to 0·7 p.c. of nickel. Steels with 17–18 p.c. of chromium and 7 p.c. or more of nickel are not hardened by quenching and have superior corrosive resistance. A small amount of silver increases the resistance of stainless steel to sea-water.

Chromium Compounds

Chromium forms three well-known series of compounds :

(i) **Chromous compounds** CrX_2 containing 2-valent chromium and resembling manganous and ferrous salts ; CrO is strongly basic ;

(ii) **Chromic compounds** CrX_3 containing 3-valent chromium and resembling ferric salts ; Cr_2O_3 is weakly basic and amphoteric ;

(iii) **Chromium trioxide** CrO_3, containing 6-valent chromium and analogous to sulphur trioxide ; CrO_3 is strongly acidic, forming **chromates** and **dichromates.**

The colours of the corresponding hydrated ions are : $Cr^{\cdot\cdot}$ blue, $Cr^{\cdot\cdot\cdot}$ violet or green, CrO_4'' yellow, Cr_2O_7'' orange-red.

Univalent chromium seems to be formed, together with 5-*valent chromium*, by the action of $CrCl_2$ on phenyl magnesium bromide in ether, as the solution evolves hydrogen after precipitation of bivalent chromium as acetate (Hein, etc., 1927–32) : $4CrCl_2 + 4C_6H_5MgBr = 3CrCl + (C_6H_5)_4CrCl + 2MgCl_2 + 2MgBr_2$.

Chromous Compounds

A blue solution of a chromous salt, formed by reducing a chromic salt in acid solution with nascent hydrogen : $Cr^{\cdot\cdot\cdot} + H \rightleftharpoons Cr^{\cdot\cdot} + H^{\cdot}$, is a powerful reducing agent ; the reaction is reversible and chromous salts in acid solution evolve hydrogen, especially in contact with platinum, although they do not react with pure water.

Expt. 1.—Place 50 g. of pure granulated zinc and 10 g. of finely powdered potassium dichromate in a flask (Fig. 307). Add a mixture of 200 c.c. of concentrated hydrochloric acid and 100 c.c. of water. A violent reaction occurs, the liquid first becoming green ($CrCl_3$) and then blue ($CrCl_2$). The liquid is rapidly drawn by suction through an asbestos filter into a saturated solution of 92 g. of sodium acetate crystals. A red precipitate of **chromous acetate** $Cr(CH_3{\cdot}CO_2)_2$ is thrown down. This is fairly stable : it is washed by decantation with water saturated with carbon dioxide in a closed flask.

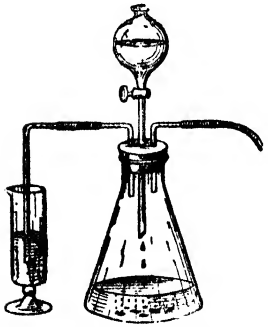


Fig. 307.—Preparation of chromous chloride.

The second part of the preparation is more difficult. The air is expelled from the flask by hydrogen and the solid dissolved in concentrated hydrochloric acid. A blue solution of chromous chloride is formed. This is cooled in ice and a current of hydrogen chloride gas passed in. **Chromous chloride** $CrCl_2{,}4H_2O$ is precipitated in blue needles (Recoura, *Ann. Chim.*, 1887, **10**, 5 ; Hume and Stone, *J.A.C.S.*, 1941, **63**, 1200).

Chromous chloride $CrCl_2$ is obtained anhydrous in white deliquescent needles (perhaps hexagonal, like $FeCl_2$) by heating chromium in dry hydrogen chloride, or anhydrous chromic chloride in dry hydrogen : $2CrCl_3 + H_2 = 2CrCl_2 + 2HCl$

(at higher temperatures chromium is formed). Fused chromous chloride is an electrolyte. The vapour density between 1300° and 1600° indicates appreciable association: $Cr_2Cl_4 \rightleftharpoons 2CrCl_2$. Hydrates with 2 (green), 3 (light blue), and 4 (blue and green forms) H_2O are known, and unstable $H_2[Cr_3Cl_8],13H_2O$ is precipitated from a concentrated solution by hydrogen chloride gas.

Chromous fluoride CrF_2 is a white almost insoluble solid, m.p. 1100°, formed by the action of hydrogen fluoride on red-hot chromium or on chromous chloride at room temperature.

Chromous bromide $CrBr_2$ and **chromous iodide** CrI_2 are white solids formed by passing hydrogen over the heated chromic compounds. They are soluble in water to blue solutions.

Chromous oxide CrO is formed as a black powder by the action of air or dilute nitric acid on chromium amalgam. **Chromous hydroxide** $Cr(OH)_2$ is formed as a brownish-yellow precipitate from alkali hydroxide and a chromous salt solution. It rapidly oxidises in air and when heated it evolves hydrogen: $2Cr(OH)_2 = Cr_2O_3 + H_2 + H_2O$, so that chromous oxide is not formed in this way.

Chromous carbonate $CrCO_3$ is obtained as a grey precipitate on adding alkali carbonate to a chromous salt solution. Excess of alkali carbonate forms very stable yellow or red crystalline complex salts, $K_2[Cr(CO_3)_2],3H_2O$ and $Na_2[Cr(CO_3)_2],10H_2O$, which on boiling with water evolve hydrogen.

Chromous oxalate CrC_2O_4,H_2O is yellow and sparingly soluble; when moist it absorbs only very little oxygen from the air and when dry it is the most stable chromous salt.

Chromous sulphate $CrSO_4,7H_2O$ is obtained in fine blue monoclinic crystals, isomorphous with ferrous sulphate, by dissolving the acetate or metal in dilute sulphuric acid and cooling. It forms blue double salts, *e.g.* $K_2[Cr(SO_4)_2],6H_2O$, isomorphous with ferrous, vanadous and manganous compounds. Ammoniacal chromous sulphate solution absorbs acetylene; the aqueous solution absorbs oxygen and nitric oxide.

Chromic Compounds

The **chromic salts** are stable, contain 3-valent chromium, and correspond with the very stable green chromic oxide Cr_2O_3. This is less basic than chromous oxide CrO and also forms *chromites* with strong bases. The chromic salts mostly exist in two forms: (i) a form which is *violet* in hydrated crystals or in solution, containing the chromic ion $Cr(H_2O)_6^{\cdots}$, and (ii) one or more *green* forms in which part or all of the chromium is in a complex ion. Tervalent chromium forms very stable complex anions with very weak acids and there is a series of ammines, *e.g.* $[Cr(NH_3)_6]Cl_3$.

Black **chromic hydride** CrH_3 is formed by passing hydrogen into a suspension of anhydrous chromic chloride in phenyl magnesium bromide in ether (Weichselfelder and Thiede, 1926).

Chromic fluoride CrF_3 is formed in dark green rhombic needles, m.p. 1100°, by passing hydrogen fluoride over $CrCl_3$ at 1200°, when it sublimes. A violet

hydrate $CrF_3,6H_2O$ or $[Cr(H_2O)_6]F_3$ is precipitated by concentrated potassium fluoride from a saturated solution of chromic nitrate. It is sparingly soluble and hydrolysed ; it forms a violet solution in hydrochloric acid. Other hydrates with 9, 4, $3\frac{1}{2}$ and $3H_2O$, and green complex salts $K_3[CrF_6]$, $K_2[Cr(H_2O)F_5]$ and $Tl_3[Cr_2F_9]$ are known.

Small quantities of brown amorphous **chromium tetrafluoride** CrF_4, giving a blue vapour, and bright red liquid **chromium pentafluoride** CrF_5 are formed by the action of fluorine on chromium (von Wartenberg, 1941).

Chromic chloride $CrCl_3$ is obtained anhydrous as a sublimate of peach-blossom coloured scaly rhombohedral crystals by passing chlorine over heated chromium or a mixture of chromic oxide and carbon at a red heat :

$$Cr_2O_3 + 3C + 3Cl_2 = 2CrCl_3 + 3CO.$$

Matignon and Bourion (1904) obtained it by passing sulphur chloride vapour alone or mixed with chlorine over chromic oxide heated below redness : $4Cr_2O_3 + 3S_2Cl_2 + 9Cl_2 = 8CrCl_3 + 6SO_2$. It is also formed by heating the hydrate in hydrogen chloride above 250°. The crystals volatilise at 1065° and the vapour density at 1200°–1300° corresponds with $CrCl_3$: at higher temperatures dissociation occurs : $2CrCl_3 \rightleftharpoons 2CrCl_2 + Cl_2$. The crystals are almost insoluble in cold water and even in boiling concentrated sulphuric acid, but rapidly dissolve in water in presence of a trace of chromous chloride (or a reducing agent such as $SnCl_2$ or CuCl), giving a green solution (Peligot, 1844).

There are *three crystalline hexahydrates* of chromic chloride, one greyish-blue and two green, which Werner formulated as :

greyish-blue (monoclinic)	$[Cr(H_2O)_6]Cl_3$,
light green	$[Cr(H_2O)_5Cl]Cl_2 + H_2O$,
dark green (rhombohedral)	$[Cr(H_2O)_4Cl_2]Cl + 2H_2O$.

The *dark green* form (Peligot, 1845) is easily made by boiling chromic anhydride with concentrated hydrochloric acid : $2CrO_3 + 12HCl = 2CrCl_3 + 3Cl_2 + 6H_2O$. The solution is evaporated till its weight corresponds with less water than $CrCl_3,6H_2O$ and is then diluted to this weight and cooled. The crystals are re-dissolved in a little water and hydrogen chloride and ether added, when small emerald-green crystals separate.

The *greyish-blue* chloride (Recoura, 1887) is made by dissolving the crude dark green chloride in its own weight of water, boiling for half an hour under a reflux, cooling below 0°, and passing in excess of hydrogen chloride. Greyish-blue crystals, dissolving in cold water to a greenish-blue solution, separate.

The *light green* chloride (Bjerrum, 1906) is precipitated on adding ether saturated with hydrogen chloride to the filtrate from the greyish-blue chloride and passing in hydrogen chloride at 10°. (All three forms have been successfully made by the author by these methods.)

In solution the greyish-blue chloride gives three chloride ions, since all the chlorine is precipitated by silver nitrate. The light green form readily loses one molecule of water and in solution gives two chloride ions, only two-thirds of the chlorine being precipitated by silver nitrate. The dark green form readily loses two molecules of water and in solution gives primarily only one

chloride ion, only one-third of the chlorine being precipitated by silver nitrate in presence of a little nitric or sulphuric acid when the silver chloride is at once filtered (Werner and Gubser, *Ber.*, 1901, **34**, 1579).

Other hydrates are described, and a heliotrope-coloured solid $HCrCl_4,xH_2O$ is formed by the action of hydrogen chloride gas on a concentrated solution of the dark green chloride (Partington and Tweedy, *J.C.S.*, 1927, 2899).

Chromic bromide $CrBr_3$ is obtained anhydrous in greenish-black hexagonal crystals by passing bromine vapour over heated chromium or a mixture of chromic oxide and carbon ; like $CrCl_3$ it dissolves in cold water only in presence of a reducing agent. Violet and green forms of the hexahydrate are probably $[Cr(H_2O)_6]Br_3$ and $[Cr(H_2O)_4Br_2]Br,2H_2O$. **Chromic iodide** CrI_3 is formed in red crystals by passing iodine vapour diluted with nitrogen over red-hot chromium ; a dark violet hydrate $CrI_3,9H_2O$ or $[Cr(H_2O)_3(H_4O_2)_3]I_3$ is formed by mixing violet chromic sulphate with concentrated barium iodide and saturating the cooled filtrate with hydrogen iodide ; it evolves hydrogen iodide on keeping.

Chromic oxide is formed as a green powder by heating chromic hydroxide : $2Cr(OH)_3 = Cr_2O_3 + 3H_2O$, ammonium dichromate : $(NH_4)_2Cr_2O_7 = Cr_2O_3 + N_2 + 4H_2O$, or sodium dichromate with sulphur in an iron pot and washing out the sodium sulphate from the residue : $Na_2Cr_2O_7 + S = Na_2SO_4 + Cr_2O_3$. A fine green oxide is produced by gently heating mercurous chromate : $4Hg_2CrO_4 = 8Hg + 2Cr_2O_3 + 5O_2$. Dark green or black hard hexagonal crystals, isomorphous with Al_2O_3 and Fe_2O_3, are formed by fusing the oxide with calcium carbonate and boron trioxide, by igniting a mixture of potassium dichromate and sodium chloride, or by passing chromyl chloride vapour through a red-hot tube : $4CrO_2Cl_2 = 2Cr_2O_3 + O_2 + 4Cl_2$.

The crystalline oxide or that formed by igniting the hydroxide or ammonium dichromate is practically insoluble in acids, except hot 70 p.c. perchloric acid, which oxidises it to CrO_3 ; it may be dissolved by fusing with potassium hydrogen sulphate or sodium peroxide, or by heating with alkaline permanganate solution, when a chromate is formed and manganese dioxide precipitated : $Cr_2O_3 + 2MnO_4' + 2OH' = 2CrO_4'' + 2MnO_2 + H_2O$.

The incandescence at a higher temperature of chromic oxide formed by gently heating the hydroxide is also shown by ferric oxide (p. 857), alumina, titanium dioxide, and especially zirconium dioxide. It was noticed by Berzelius in 1816. There is no change in the X-ray spectra after glowing (Hedvall, 1922), and the change is probably due to a reduction of specific surface due to the coalescence of primary particles (Wöhler, 1912). The solid becomes denser and less reactive.

Chromic oxide (m.p. over 2000°) is very refractory but dissolves in fused borax or glass giving a green colour which becomes blue in presence of strontium ; this is used in tinting glass and painting porcelain. A pink glaze is formed with a mixture of chromic and stannic oxides (Malaguti, 1836). Chromic oxide is used as a permanent green oil paint (*chrome green* ; now

sometimes replaced by lead chromate and Prussian blue, which is less permanent).

Chromic hydroxide is formed as a pale greyish-green flocculent precipitate from a chromic salt solution and alkali hydroxide or ammonia. It slowly " ages " and changes its properties on standing in contact with the solution. A pale blue precipitate is formed from a violet chromic salt solution and ammonia in the cold.

According to Siewert (1861) pure chromic hydroxide is precipitated by ammonia from *boiling* solutions of chromic salts. In cold solutions the precipitate contains an ammonium salt, and if potassium or sodium hydroxide is used, or if alkali salts are present, it contains alkali which cannot be removed by washing. With excess of hot concentrated ammonia, especially in presence of large amounts of ammonium salts, **chromammines**, *e.g.* $[CrCl(NH_3)_4(H_2O)]Cl_2$, are formed and some chromium dissolves with a pink coloration.

Although, like aluminium and ferric hydroxides, chromic hydroxide probably exists, the composition of the precipitate depends on the extent of drying, *e.g.* $Cr_2O_3,2H_2O$ or $Cr_2O(OH)_4$ when dried over sulphuric acid, and it is amorphous to X-rays. Simon (1929) reported a break corresponding with $Cr(OH)_3$ on the dehydration vapour pressure curve, but Hackspill and Kieffer (1930) did not find it. The hydrate Cr_2O_3,H_2O or CrO(OH), formed by heating the fresh gel in an autoclave, is crystalline and gives an X-ray pattern (Simon, 1929).

By fusing equimolecular amounts of potassium dichromate and boric acid and washing, a brilliant green powder called *Guignet's green*, used as a pigment, is obtained. It is usually formulated as $Cr_2O_3,2H_2O$ or $Cr_2O(OH)_4$, but normally contains boric acid, although $Cr_2O_3,2{\cdot}14H_2O$ free from boric acid was obtained by Simon (1929).

Freshly precipitated chromic hydroxide readily dissolves in alkali hydroxide solution to a clear deep green solution which probably contains a **chromite**, *e.g.* $Na_2Cr_2O_4$ or $NaCrO_2$ (cf. ferrite), although colloidal chromium hydroxide may be present and is precipitated on boiling. Solid alkali chromites, *e.g.* $Na_2Cr_2O_4,8H_2O$ (Scholder and Pätsch, 1934) are known, and crystalline chromites $M(CrO_2)_2$, where M = Mg, Ba, Zn, Cd and Cu, and Cu^ICrO_2, are formed by fusion reactions. Chrome ironstone is ferrous chromite $FeCr_2O_4$.

Dark green **colloidal chromic hydroxide**, formed by dialysing a solution of the freshly precipitated hydroxide in chromic chloride solution, can be boiled but is precipitated by salts.

Chromic hydroxide is not a strong base and no normal chromic carbonate is known; a bluish-grey hydrated **basic carbonate** is precipitated by alkali carbonate, and is soluble in excess.

A green solution of **chromic acetate** $Cr(CH_3COO)_3$, used as a mordant, is formed on dissolving chromic hydroxide in acetic acid.

Chromium nitride CrN is a brown or black powder (cubic) formed by heating finely divided chromium in nitrogen or ammonia, or anhydrous chromic chloride in ammonia. It is stable to acids (except aqua regia and concentrated sulphuric acid, which dissolve it slowly) and even fused alkalis, but deflagrates with fused

KNO_3 and dissolves in hypochlorite solution with evolution of nitrogen and formation of chromate.

Chromic nitrate is formed by dissolving precipitated chromic hydroxide in excess of dilute nitric acid and crystallises in purple monoclinic prisms of $Cr(NO_3)_3,9H_2O$. It is stable in the violet form and the solution only slowly becomes green on heating, recovering the reddish-violet colour on cooling. The chloride and sulphate solutions readily become green on heating and only very slowly pass into the violet forms in the cold.

Chromic cyanide $Cr(CN)_3$ is precipitated from a chromic salt solution by potassium cyanide; the white precipitate becomes bluish-grey. It is only slowly soluble in excess of cyanide. **Potassium chromicyanide** $K_3Cr(CN)_6$ forms bright yellow monoclinic crystals isomorphous with ferricyanide from a solution of chromic acetate poured into excess of boiling potassium cyanide solution. The free acid $H_3Cr(CN)_6$ is formed in red solution by the action of H_2S on a suspension of the lead or silver salt. **Potassium chromithiocyanate** $K_3Cr(SCN)_3,4H_2O$ in dark violet crystals, and other salts, and the free acid $H_3Cr(SCN)_6$, are known. These compounds emphasise the resemblance between 3-valent chromium and iron.

Chromic phosphate $CrPO_4$ is formed as an amorphous violet precipitate from chromic salts and sodium phosphate. On standing for a day or two in contact with the solution this is converted into a violet crystalline hexahydrate $CrPO_4,6H_2O$. On standing for a week in the solution, the amorphous precipitate forms a green *amorphous* tetrahydrate $CrPO_4,4H_2O$. A green *crystalline* tetrahydrate is formed by boiling the violet hexahydrate with water for half an hour, and a green dihydrate $CrPO_4,2H_2O$ by boiling the other hydrates with acetic anhydride. On heating, all the hydrates give a black powder of $CrPO_4$ (Joseph and Rae, *J.C.S.*, 1917, **111**, 196).

Chromic sulphide Cr_2S_3 is obtained in green or black crystals or powder by heating sulphur with chromium, or $CrCl_3$ in H_2S. It is not decomposed by water or acids, but is not formed on adding a solution of ammonium sulphide to a chromic salt, when only the hydroxide is precipitated:

$$2CrCl_3 + 6H_2O + 3(NH_4)_2S = 2Cr(OH)_3 + 6NH_4Cl + 3H_2S.$$

Thiochromites are analogous to chromites; red crystals of $NaCrS_2$ are formed by fusing potassium chromate with a large excess of sodium carbonate and sulphur; by boiling it with metal salt solutions brown or black insoluble metal thiochromites, *e.g.* $Cu(CrS_2)_2$, $Zn(CrS_2)_2$, $Fe(CrS_2)_2$ are formed.

Chromic sulphate is obtained in violet octahedral crystals, $Cr_2(SO_4)_3,17$ or $18H_2O$, by allowing a mixture of chromic hydroxide dried at 100° and the calculated weight of concentrated sulphuric acid to stand for some weeks in a loosely-stoppered bottle, or by precipitating the solution with a little alcohol (cf. Graham, *Amer. Chem. J.*, 1912, **48**, 145). There are also hydrates with 9 and $3H_2O$. The rose-red anhydrous sulphate, insoluble in water, is formed by heating the hydrate in a current of carbon dioxide at 280° and then at about 400° till the weight is constant.

By heating potassium dichromate or chrome alum with concentrated sulphuric acid, an olive-coloured acid sulphate $2Cr_2(SO_4)_3,H_2SO_4$ completely insoluble in water and acids is formed.

A green variety of chromic sulphate is formed by heating the violet crystals $Cr_2(SO_4)_3,18H_2O$ at 90° until they have the composition $Cr_2(SO_4)_3,6H_2O$. The solution is not precipitated by alkalis or barium chloride, and is capable of "masking" the reaction of other sulphate ions. On standing, the solution is slowly transformed into a violet solution, completely precipitated by barium chloride. Werner represents the forms as follows: *violet* $[Cr_2(H_2O)_{12}](SO_4)_3+6H_2O$; *green* $[Cr_2(SO_4)_3(H_2O)_6]$. A number of complex chromi-sulphuric acids, *e.g.* $H_2[Cr_2(SO_4)_4]$ which gives no reactions of Cr''' or SO_4'' ions, and other salts are known.

The constitution of green chromic sulphate solutions is very complex and some hydrolysis occurs. According to Recoura (1887) if the acid formed by hydrolysis is nearly neutralised by alkali and an acid then added a violet solution is rapidly formed.

Chromic sulphate forms with alkali sulphates (Na, K, Rb, Cs, NH_4, also Tl^I) **chrome alums** $M^ICr(SO_4)_2,12H_2O$. Common or **potassium chrome alum** $KCr(SO_4)_2,12H_2O$ is obtained (Mussin-Puschkin, 1798) by reducing a solution of potassium dichromate acidified with sulphuric acid with sulphur dioxide, alcohol or oxalic acid, or electrolytically, below 70°. It forms deep purple octahedral crystals. The **ammonium chrome alum** $(NH_4)Cr(SO_4)_2,12H_2O$ is bright violet-blue.

EXPT. 2.—Dissolve 20 g. of $K_2Cr_2O_7$ in 150 c.c. of hot water, cool, and add 4 c.c. of conc. H_2SO_4. Pass sulphur dioxide slowly into the well-cooled solution until the colour, which changes from red to brown and then olive-green, becomes greenish-blue. Set the solution aside in a loosely-covered dish until crystals form: $K_2Cr_2O_7+H_2SO_4+3SO_2=K_2SO_4+Cr_2(SO_4)_3+H_2O$.

In another method, 5 c.c. of absolute alcohol is added with constant stirring to a solution of 15 g. of $K_2Cr_2O_7$ and 12·5 c.c. of conc. H_2SO_4 in 100 c.c. of water, the liquid being cooled in ice.

Chrome alum is formed as a by-product in the oxidation of anthracene to anthraquinone with sulphuric acid and potassium dichromate. It is used in dyeing and calico-printing and in chrome-tanning.

A solution of chrome alum in cold water is dull bluish-red; it becomes green at 70°. From the violet solution barium chloride precipitates all the sulphate, but only half that in the green solution (Whitney, *J.A.C.S.*, 1899, **21**, 1075). On long standing in the cold the green solution recovers the violet colour.

CHROMIUM TRIOXIDE AND CHROMATES

Chromium trioxide CrO_3 is obtained by the action of concentrated sulphuric acid on a solution of a chromate or dichromate (Mussin-Puschkin, 1798). It is a red crystalline solid, sometimes called "chromic acid" (of which it is the anhydride; H_2CrO_4 is unknown). A solution of CrO_3 is red and strongly acid, and the colour, freezing point and conductivity suggest that it contains **dichromic acid** $H_2Cr_2O_7$, which is not known in the pure state (Ostwald, 1888).

Perhaps the acid H_2CrO_4 ionises into $H^·$ and $HCrO_4'$ and the acid chromate ion forms the dichromate ion (Sherrill, *J.A.C.S.*, 1907, **29**, 1614):

$2HCrO_4' \rightleftharpoons Cr_2O_7'' + H_2O$. In concentrated solutions Cr_3O_{10}'' and Cr_4O_{13}'', formed by addition of CrO_3 to Cr_2O_7'', may be present.

EXPT. 3.—Dissolve 50 g. of $K_2Cr_2O_7$ in 85 c.c. of water and to the cooled solution add slowly 70 c.c. of concentrated H_2SO_4. Allow to stand for twelve hours and pour the liquid off the crystals of acid potassium sulphate: $K_2Cr_2O_7 + 2H_2SO_4 = 2CrO_3 + 2KHSO_4 + H_2O$. Heat to 85°, add 25 c.c. of sulphuric acid and sufficient water just to dissolve the CrO_3 separating. Allow to stand twelve hours and decant the liquid from the crystals of CrO_3. Wash the latter with pure nitric acid in a Buchner funnel containing asbestos, and heat at 60°–80° in a current of pure dry air in a tube to remove adhering nitric acid.

Bunsen (1868) added 100 g. of sulphuric acid to 20 g. of $K_2Cr_2O_7$ in 200 c.c. of water; after 24 hours the long needles of CrO_3 which separated were treated as above.

Chromium trioxide forms deliquescent lustrous red rhombic prisms, s. g. 2·7. It melts at 198° to a dark red liquid, solidifying on cooling to a reddish-black mass with a metallic lustre. It begins to decompose at 200°: $4CrO_3 = 2Cr_2O_3 + 3O_2$, but usually a little sublimes; decomposition is complete at 420° (Honda and Soné, 1914). Chromium trioxide is a very powerful oxidising agent. Alcohol dropped on it ignites, ether is violently oxidised, and the concentrated solution is reduced by sugar, oxalic acid, paper, cork, etc. It oxidises sulphur dioxide, hydrogen sulphide, stannous chloride, arsenious oxide, ferrous salts, iodides, etc. In acid solutions the reduction always proceeds to the stage of a chromic salt: $2CrO_3 = Cr_2O_3 + 3O$.

$2CrO_3 + 3SO_2 = Cr_2(SO_4)_3$ (some dithionate is formed).

$2CrO_3 + 3H_2S + 3H_2SO_4 = Cr_2(SO_4)_3 + S + 6H_2O$.

$2CrO_3 + 3SnCl_2 + 12HCl = 2CrCl_3 + 3SnCl_4 + 6H_2O$.

$4CrO_3 + 3As_2O_3 + 12HCl + 3H_2O = 4CrCl_3 + 6H_3AsO_4$.

$2CrO_3 + 6FeSO_4 + 6H_2SO_4 = Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 6H_2O$.

$K_2Cr_2O_7 + 6FeSO_4 + 7H_2SO_4 = Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + K_2SO_4 + 7H_2O$.

$K_2Cr_2O_7 + 6KI + 7H_2SO_4 = Cr_2(SO_4)_3 + 4K_2SO_4 + 3I_2 + 7H_2O$.

A solution of potassium dichromate acidified with sulphuric acid is often used as an oxidising agent (*e.g.* for converting alcohol to acetaldehyde); a solution of chromium trioxide in glacial acetic acid (which is not oxidised) is also used.

A persulphate on boiling in solution in presence of silver ion as a catalyst oxidises a chromic salt to chromic acid, which is also formed at a lead dioxide anode in the electrolysis of a chromic salt in presence of fluoride. In *alkaline* solution chromic hydroxide is easily oxidised to a chromate by manganese dioxide, lead dioxide, hypochlorite, sodium peroxide and even mercuric oxide: $Cr^{+++} + 6OH^- + O = CrO_4^{--} + 3H_2O + e$. The oxides MnO_2 and PbO_2 are reduced to Mn_2O_3 and PbO.

Chromates.—Chromic acid in its salts shows close analogies to sulphuric acid and its formula may be written $CrO_2(OH)_2$. It forms **normal chromates** (*e.g.* K_2CrO_4) and **dichromates** (*e.g.* $K_2Cr_2O_7$), analogous to sulphates and disul-

phates. Acid chromates, *e.g.* $KHCrO_4$, are not known, but by the action of excess of CrO_3 or by boiling the dichromate with nitric acid, **trichromates** (*e.g.* $K_2Cr_3O_{10}$ or $K_2O,3CrO_3$) and **tetrachromates** (*e.g.* $K_2Cr_4O_{13}$ or $K_2O,4CrO_3$) are formed as red crystals. The chromates are isomorphous with sulphates, selenates, molybdates and tungstates of corresponding formulae.

Chromates (and dichromates) are manufactured from chromite (or chrome ironstone) $Fe(CrO_2)_2$ or $FeCr_2O_4$. The finely powdered chromite is strongly heated with alkali or alkali carbonate with free exposure to air ; the chromium is slowly oxidised to a chromate and the iron to ferric oxide :

$$4FeCr_2O_4 + 16NaOH + 7O_2 = 2Fe_2O_3 + 8Na_2CrO_4 + 8H_2O$$
$$4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 = 2Fe_2O_3 + 8Na_2CrO_4 + 8CO_2.$$

Oxidation is more rapid with a mixture of alkali carbonate and potassium nitrate or chlorate, or with sodium peroxide :

$$2FeCr_2O_4 + 4K_2CO_3 + 7KNO_3 = Fe_2O_3 + 4K_2CrO_4 + 7KNO_2 + 4CO_2$$
$$6FeCr_2O_4 + 12K_2CO_3 + 7KClO_3 = 3Fe_2O_3 + 12K_2CrO_4 + 7KCl + 12CO_2$$
$$2FeCr_2O_4 + 7Na_2O_2 = Fe_2O_3 + 4Na_2CrO_4 + 3Na_2O.$$

Expt. 4.—Fuse a little powdered chromite with sodium peroxide in a nickel crucible. Extract the cooled mass with water. A yellow solution of sodium chromate is obtained. This is converted into a red solution of the dichromate when sulphuric acid is added.

On the large scale a **dichromate** is made by adding sulphuric acid to the solution of potassium (or sodium) chromate :

$$2K_2CrO_4 + H_2SO_4 = K_2Cr_2O_7 + K_2SO_4 + H_2O.$$

In a modern process (Sofianopoulos, *J.S.C.I.*, 1930, **49**, 279 T.) a mixture of 340 lb. of finely powdered chromite, 270 lb. of sodium carbonate and 360 lb. of quicklime is heated to redness in a reverberatory furnace with free exposure to air, when all the carbon dioxide is expelled and sodium chromate is formed. The function of the quicklime is to keep the mass porous and prevent fusion. Some chromite remains unattacked and a little calcium chromate, not readily converted into a soluble chromate, is formed. The sodium chromate is extracted with water, concentrated sulphuric acid is added to the solution, and the sodium sulphate which separates is removed. The solution is concentrated to s. g. 1·7 and deliquescent red crystals of **sodium dichromate** $Na_2Cr_2O_7,2H_2O$ slowly separate.

The sodium dichromate is much cheaper and more soluble, but may be converted into potassium dichromate by reaction in solution with potassium chloride. Chromates and dichromates are used as oxidising agents, as mordants in dyeing, and in preparing insoluble pigments.

Normal **potassium chromate** K_2CrO_4 is formed in lemon-yellow rhombic crystals, m.p. 968·3°, isomorphous with potassium sulphate K_2SO_4, by the action of the calculated amount of potassium hydroxide or carbonate on a solution of chromium trioxide or potassium dichromate : $K_2Cr_2O_7 + 2KOH = 2K_2CrO_4 + H_2O$, evaporation and crystallisation. The yellow solution is alkaline :

$$CrO_4'' + H_2O \rightleftharpoons HCrO_4' + OH'.$$

Dichromate solutions are orange-red and acid :

$$Cr_2O_7'' + H_2O \rightleftharpoons 2CrO_4'' + 2H^{\cdot}.$$

Potassium dichromate $K_2Cr_2O_7$ may be obtained by adding the requisite amount of sulphuric acid to a saturated solution of the normal chromate, and crystallises on cooling in garnet-red triclinic crystals, m.p. 398°.

A monoclinic form is produced at 237° and the solid formed from the melt crumbles to a crystalline powder below this temperature (Robinson, Stephenson and Briscoe, *J.C.S.*, 1925, **127**, 547).

The solubilities in 100 pts. of water are :

	0°	30°	60°	105·6°	104·8°
K_2CrO_4 -	- 57·11	65·13	74·60	88·8 (b.p.)	—
$K_2Cr_2O_7$ -	- 4·64	18·09	46·10	—	106·2 (b.p.)

Both salts are non-deliquescent and crystallise without water.

Sodium chromate $Na_2CrO_4,10H_2O$ (monoclinic) and **sodium dichromate** $Na_2Cr_2O_7,2H_2O$ (monoclinic) are both deliquescent. The dichromate is made on the large scale. A solution of sodium chromate is formed by triturating moist chromic hydroxide with sodium peroxide.

Ammonium chromate $(NH_4)_2CrO_4$ (monoclinic) is unstable and tends to lose ammonia to form dichromate ; it is obtained by crystallising solutions containing excess of ammonia. **Ammonium dichromate** $(NH_4)_2Cr_2O_7$ is readily obtained by adding ammonia to the requisite amount of chromium trioxide in solution. It forms orange-red monoclinic crystals which decompose violently on heating (p. 542) : $(NH_4)_2Cr_2O_7 = Cr_2O_3 + N_2 + 4H_2O$.

All soluble chromates are poisonous. Metallic chromates, if soluble, are formed from the oxides or carbonates and chromic acid, if insoluble by double decomposition. The most important sparingly soluble chromates are :

Silver chromate Ag_2CrO_4, brick-red, rather difficultly soluble in acids and ammonia.

Barium chromate $BaCrO_4$, yellow, insoluble in acetic acid, used in the gravimetric determination of barium or chromate, soluble in hydrochloric, nitric and chromic acids.

Zinc chromate (basic) $Zn_2(OH)_2CrO_4,H_2O$, a yellow pigment.

Mercurous chromate Hg_2CrO_4, a red crystalline powder.

Lead chromate $PbCrO_4$ (*chrome-yellow*), a pigment, probably the least soluble lead salt ($1·2 \times 10^{-5}$ g./lit.) ; it is insoluble in ammonium acetate (which dissolves $PbSO_4$), and is also (incompletely) precipitated by dichromate :

$$Cr_2O_7'' + Pb^{\cdot\cdot} \rightleftharpoons PbCrO_4 + CrO_3 ;$$

it is sparingly soluble in dilute nitric acid but readily in alkali :

$$PbCrO_4 + 4NaOH = Na_2PbO_2 + Na_2CrO_4 + 2H_2O.$$

Basic lead chromate $PbCrO_4,PbO$ (*chrome red*), a bright red pigment formed by digesting $PbCrO_4$ with cold dilute sodium hydroxide solution ; mixed with $PbCrO_4$ it forms *chrome orange*.

Basic bismuth dichromate $(BiO)_2Cr_2O_7$, orange yellow.

Chromium dioxide CrO_2, probably **basic chromic chromate** Cr_2O_3,CrO_3 or $(Cr^{III}O)_2Cr^{VI}O_4$, is a black powder formed by gently heating chromium trioxide, chromic nitrate or ammonium dichromate, or by precipitating a chromic salt with a soluble chromate (Ridley, *Chem. News*, 1924, **129**, 35). It has a variable composition and one crystalline form (obtained by passing CrO_2Cl_2 vapour through a tube at 400°) is Cr_5O_9 (Cameron, Harbard and King, *J.C.S.*, 1939, 55, who regard it as a " non-stoichiometric " oxide : see p. 253). When heated in chlorine it forms Cr_2O_3 and chromyl chloride CrO_2Cl_2.

Chromyl chloride.—Just as sulphur forms sulphuryl chloride SO_2Cl_2 derived from sulphuric acid $SO_2(OH)_2$, chromium and the other Group VI metals form **oxychlorides** containing bivalent radicals $=XO_2$:

chromyl chloride CrO_2Cl_2	**tungstyl chloride** WO_2Cl_2
molybdyl chloride MoO_2Cl_2	**uranyl chloride** UO_2Cl_2

The chromium compound (Berzelius, 1824, and Thomson, 1825) is a red liquid, the others are yellow solids.

Chromyl fluoride CrO_2F_2 was described as a deep red volatile liquid formed by distilling a mixture of potassium dichromate, calcium fluoride and concentrated sulphuric acid in a lead retort (Unverdorben, 1824), but as formed by the action of fluorine on CrO_2Cl_2 it is a brown-red solid, changing into a dirty white polymer (von Wartenberg, 1941).

Chromyl chloride is prepared by distilling a mixture of potassium dichromate and sodium chloride with concentrated (preferably fuming) sulphuric acid :

$$K_2Cr_2O_7 + 4NaCl + 6H_2SO_4 = 2CrO_2Cl_2 + 2KHSO_4 + 4NaHSO_4 + 3H_2O.$$

EXPT. 5.—A finely powdered dry mixture of 25 g. of sodium chloride and 40 g. of potassium dichromate is placed in a large dry stoppered retort and 40 c.c. of fuming sulphuric acid added in small portions. Reaction begins without heating and chromyl chloride distils into a cooled dry receiver. The mixture is gently heated when reaction slackens. (Moles and Gómez, *Z. phys. Chem.*, 1912, **80**, 513). Ordinary concentrated sulphuric acid gives a good yield but the product is less pure. Fusing the NaCl and $K_2Cr_2O_7$ together is unnecessary. The chromyl chloride is purified by distillation and kept in a sealed tube.

The deep red vapour condenses to a very dark red, nearly black, liquid, b.p. 116·7°, m.p. −96·5°, s. g. 1·91, very like bromine. The vapour density corresponds with CrO_2Cl_2.

In another preparation (Law and Perkin, *J.C.S.*, 1907, **91**, 191) chromium trioxide is dissolved in cold concentrated hydrochloric acid, the liquid is cooled, and concentrated sulphuric acid added in small portions. Liquid chromyl chloride separates ; it is run off and distilled : $CrO_3 + 2HCl = CrO_2Cl_2 + H_2O$. It is also formed by the action of gaseous hydrogen chloride on chromium trioxide.

Chromyl chloride is violently hydrolysed by water : $CrO_2Cl_2 + H_2O = CrO_3 + 2HCl$. It is a powerful oxidising agent, exploding in contact with phosphorus (cf. Br_2) and inflaming sulphur, ammonia, alcohol, and many organic substances. Bromides and iodides do not form similar compounds when distilled with

potassium dichromate and sulphuric acid, but the free halogens are liberated. This may be used to detect chlorides in presence of bromides and iodides, since the distillate when collected in water forms chromic acid, giving a yellow precipitate with lead acetate, when chloride is present.

Chlorochromates.—When three parts of powdered potassium dichromate are dissolved in four parts of warm concentrated hydrochloric acid and a little water and the liquid cooled, or if chromyl chloride is added to a saturated solution of potassium chloride, red monoclinic crystals of **potassium chlorochromate** $KCrO_3Cl$ are formed :

$$K_2Cr_2O_7 + 2HCl = 2KCrO_3Cl + H_2O$$
$$CrO_2Cl_2 + KCl + H_2O = KCrO_3Cl + 2HCl.$$

This is called *Peligot's salt* (1833) ; it is a salt of an unknown **chlorochromic acid** [cf. chlorosulphonic acid, $SO_2(OH)Cl$] :

$CrO_2(OH)_2$	$CrO_2(OH)Cl$	CrO_2Cl_2
(hypothetical) **chromic acid.**	(hypothetical) **chlorochromic acid.**	**chromyl chloride.**

Potassium chlorochromate is partly decomposed by water and decomposes on heating with evolution of chlorine :

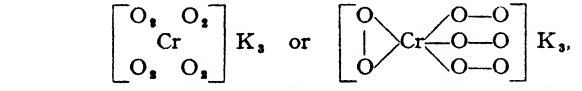
$$4CrO_2(OK)Cl = K_2Cr_2O_7 + Cr_2O_3 + 2KCl + Cl_2 + O_2.$$

By the action of cold concentrated hydrochloric acid on CrO_3 an oxychloride $CrOCl_3$ containing 5-valent chromium seems to be formed. From the solution and CsCl a salt $Cs_2[CrOCl_5]$, isomorphous with $Cs_2[NbOCl_5]$, is obtained (Weinland, etc., 1905–6).

Perchromic acid.—On mixing a solution of chromium trioxide or an acidified chromate solution with hydrogen peroxide and shaking with ether, a deep blue solution in ether is formed. This contains a higher oxygen compound of chromium called *perchromic acid* (Barreswil, 1843). On standing over dilute acid the ether slowly loses its colour and the dilute acid becomes bluish-green, from formation of a chromic salt. On standing over dilute alkali, oxygen is evolved and a yellow solution of a chromate is formed.

By the action of organic bases (aniline, pyridine, etc.) on the blue ether solution, *deep blue* explosive compounds are formed, which have been formulated as $CrO_4(OR),H_2O_2$, derived from $HCrO_5$, or as acid salts RH_2CrO_7, derived from H_3CrO_7. They seem to be addition compounds of an oxide CrO_5, and not true salts. Ammonia gives dark brown crystalline $CrO_4,3NH_3$.

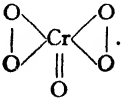
Alkaline chromate solutions and hydrogen peroxide yield *red* salts M_3CrO_8, which are formulated as



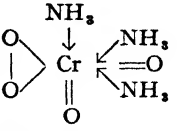
containing 5-valent chromium, which is confirmed by their paramagnetism (Tjabbes, 1933) : $2CrO_4'' + 2OH' + 7H_2O_2 = 2CrO_8''' + 8H_2O$.

With acids the red salts evolve oxygen and form blue compounds. The blue perchromic acid was formulated by Moissan as CrO_3,H_2O_2 and by Riesenfeld as H_3CrO_8. Riesenfeld (1914) by adding 97 p.c. hydrogen peroxide to CrO_3 in methyl ether at $-30°$, pouring off the blue liquid from excess of CrO_3, and

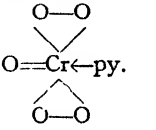
evaporating in vacuum at $-30°$, obtained dark blue explosive crystals, which he regarded as free perchromic acid $H_3CrO_8,2H_2O$ or $(HO)_4Cr(O{\cdot}OH)_3$, containing 7-valent chromium. Schwarz and Elstner (1936), however, showed that the crystals are a compound $CrO_5,(CH_3)_2O$ of methyl ether with an oxide CrO_5, which is non-acidic and a compound of 6-valent chromium :



A brown ammine $CrO_4,3NH_3$, which can be formulated as



is formed by the action of ammonia on the blue solution of " perchromic acid " in ether, oxygen being evolved. It is fairly stable and with ethylenediamine forms $[CrO_4\,en_2\,(H_2O)_2]$, and with potassium cyanide $K_2[(CN)_2CrO_4(NH_3)]$, $K_3[(CN)_3CrO_4]$ and $K_5[(CN)_5(CrO_4)_2],5H_2O$. The blue " acid " also forms a stable pyridine compound which is monomeric in benzene solution



Molybdenum

Molybdenum occurs mainly as the sulphide *molybdenite* MoS_2, s. g. 4·8, hexagonal, with a layer lattice having widely-spaced sheets of sulphur atoms (WS_2 is similar), rather like graphite, from which it was first differentiated by Scheele in 1778–9 (see p. 442). It occurs in the United States (especially Colorado), Mexico, Norway, Korea and China. The only other important ore is *wulfenite*, lead molybdate $PbMoO_4$.

On roasting in air or boiling with concentrated nitric acid, molybdenite gives a white residue of **molybdenum trioxide** MoO_3, which easily sublimes. This is an acidic oxide ; from a solution in *excess* of hot concentrated ammonia normal **ammonium molybdate** $(NH_4)_2MoO_4$ crystallises on cooling, but the common ammonium molybdate crystallising on evaporation is $(NH_4)_6Mo_7O_{24},4H_2O$ (or $3(NH_4)_2O,7MoO_3,4H_2O$), this old formula having been confirmed by Sturdivant (*J A.C.S.*, 1937, **59**, 630). The solution in dilute nitric acid containing ammonium nitrate is the " molybdate reagent " for orthophosphoric acid (p. 608), giving a canary-yellow precipitate of **ammonium phosphomolybdate**, $(NH_4)_3PO_4,12MoO_3$, $HNO_3,2H_2O$, which on drying at 160°–180° has the formula $(NH_4)_3PO_4,12MoO_3$. On ignition a black residue of approximate composition $P_2O_5,24MoO_3$ remains.

The solution of ammonium molybdate in dilute nitric acid slowly deposits yellow **α-molybdic acid** H_2MoO_4,H_2O, which on warming at 70° with water forms white **β-molybdic acid** H_2MoO_4, the two acids having different X-ray spectra and vapour pressures (Burger, 1922 ; Hüttig and Kurre, 1923).

Colloidal molybdic acid is obtained by dialysing a solution of ammonium molybdate and hydrochloric acid : it forms a gum on evaporation.

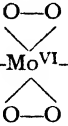
On heating any of these molybdic acids, or ammonium molybdate, white MoO_3 is obtained. On heating at 500° in hydrogen this forms the reddish-brown **dioxide** MoO_2 and at 1200° a grey powder of metallic molybdenum.

Molybdenum, discovered by Hjelm in 1782, is made commercially by strongly heating MoO_3 and carbon. The grey powder is sintered at 1000°, and hammered into rods, which are drawn into fine wires used to support the tungsten filaments in electric lamps. The metal can also be obtained (Balke, *Ind. Eng. Chem.*, 1929, **21**, 1002) by heating MoO_3 or MoO_2 in hydrogen or with aluminium (thermit process), silicon or calcium, by the electrolysis of fused salts, and by strongly heating MoS_2 in a carbon tube. It is silver-white, fairly soft, s. g. 10·2, oxidises slowly in air at ordinary temperature and rapidly on heating, and burns at 500°–600° in oxygen, forming a sublimate of MoO_3. Chlorine and bromine react at a red heat without flame; iodine, sulphur and phosphorus do not react. The metal is soluble in hot dilute nitric acid, concentrated sulphuric acid (forming a blue solution) and aqua regia, but not in hydrofluoric acid or alkali solution, although fused alkali attacks it vigorously. *Ferromolybdenum* for alloy steels is made in the electric furnace from molybdenite, pyrites, lime and coke. Steel containing 2 p.c. or more of Mo does not soften on heating and is used for high-speed lathe tools. An alloy with iron and chromium is acid-resisting.

Molybdenum forms compounds, mostly covalent, in which it has valencies of 2, 3, 4, 5 and 6, the last being most important; the compounds of lower valency are strong reducing agents. A sensitive reaction for molybdenum is the red or purple colour produced by xanthic acid.

(1) *Compounds of 6-valent* Mo (Mo^{VI}). The **hexafluoride** MoF_6 (the only halogen compound of Mo^{VI} and the only Mo fluoride known) is formed in colourless crystals by direct combination. The white solid **oxyfluorides** $MoOF_4$ and MoO_2F_2 and many **fluoxymolybdates,** $M_2[MoO_3F_2]$, $M[MoO_2F_3]$, $M_2[MoO_2F_4]$ and $M[MoOF_5]$ are known. The **oxychloride** MoO_2Cl_2 is a yellow solid formed by heating MoO_2 in chlorine; other oxychlorides ($Mo_2O_3Cl_6$, etc., but not $MoOCl_4$) are known.

The stable trioxide, the molybdic acids and molybdates, as well as complex acids and salts (*e.g.* phosphomolybdates) all contain Mo^{VI}. Hydrogen peroxide gives with a molybdate solution a red colour due to **permolybdic acid** $HMoO_4$ (Fairley, 1877) and two series of **permolybdates** are known: (i) the red crystalline K_2MoO_8, etc., giving with acids amorphous unstable permolybdic acid, and formulated $KO{\cdot}O{-}Mo^{VI}(O_2){-}O{\cdot}OK$, and (ii) a yellow series of varying composition



(Gleu, 1932; Kobosev and Sokolov, 1933).

Black **molybdenum trisulphide** MoS_3 is precipitated by acid from a solution of a **thiomolybdate** made by boiling alkali molybdate with ammonium sulphide. Many red crystalline thiomolybdates, *e.g.* K_2MoS_4, are known. **Complex oxalates** $M_2[MoO_2(C_2O_4)_2]$ and $MH[MoO_3(C_2O_4)],H_2O$ are known.

Molybdenum blue, formed by reduction of molybdates in solution by metals, H_2S, SO_2, etc., appears to contain MoO_3 and Mo_2O_5, perhaps $(Mo^{V}O)_2(Mo^{VI}O_4)_3$.

(2) *Compounds of 5-valent* Mo (Mo^{V}). The **pentachloride** $MoCl_5$ sublimes in black crystals on heating the metal or MoS_2 in dry chlorine. It has the normal vapour density, fumes in moist air, forming $Mo^{VI}O_2Cl_2$ and is decomposed by water to green $Mo^{V}OCl_3$, which forms a large number of green or blue complex salts, *e.g.* $K_2[Mo^{V}OCl_5],2H_2O$. The violet-black **pentoxide** Mo_2O_5 is formed by heating $Mo_2^{III}O(SO_4)_2 = Mo_2O_5 + 2SO_2$, or Mo powder and MoO_3 in nitrogen at 750°. The light brown **oxy-trihydroxide** $MoO(OH)_3$, the black **pentasulphide** Mo_2S_5 and

$Mo_2S_5,3H_2O$, and **molybdicyanic acid** $H_3[Mo^V(CN)_8],3H_2O$ and its salts, prepared by oxidising $H_4[Mo^{IV}(CN)_8],6H_2O$—Mo has the covalency 8 in these—are other compounds of 5-valent molybdenum.

(3) *Compounds of* 4-*valent* Mo (Mo^{IV}). **Molybdenum tetrachloride** $MoCl_4$ is formed as a brown sublimate on heating the trichloride in carbon dioxide: $2Mo^{III}Cl_3 = Mo^{IV}Cl_4 + Mo^{II}Cl_2$, or by heating MoO_2 with a solution of chlorine in CCl_4 in a sealed tube. $MoBr_4$ and possibly MoI_4 are known. The **dioxide** MoO_2, a violet powder or blue crystals, is formed by heating MoO_3 at 450° in hydrogen, or with molybdenum powder in nitrogen: it forms MoO_2Cl_2 with chlorine on heating. The **tetrahydroxide** $Mo(OH)_4$ is a black precipitate. The **disulphide** MoS_2 is molybdenite. Crystalline **molybdocyanic acid** $H_4[Mo^{IV}(CN)_8]$, $6H_2O$ is formed by the action of fuming hydrochloric acid on potassium molybdocyanide $K_4[Mo^{IV}(CN)_8],2H_2O$, which is obtained by the action of KCN on $K_3Mo^{III}Cl_6$ and gives an intense blue with ferric salts.

(4) *Compounds of* 3-*valent* Mo (Mo^{III}). **Molybdenum trichloride** $MoCl_3$, formed in copper-red crystals by passing $MoCl_5$ vapour and CO_2 through a heated tube or heating $MoCl_5$ in hydrogen at 250°, is insoluble in cold water (cf. $CrCl_3$), but a copper-red hydrate $[MoCl_3(H_2O)_3]$ giving red solutions is obtained by electrolytic reduction of a solution of MoO_3 in hydrochloric acid. By re-electrolysing, concentrating to small volume, and pouring into acetone two isomeric **oxychlorides** $[Mo^{III}OCl(H_2O)_4]$, which are *cis*- and *trans*-forms, are obtained (Wardlaw and Wormell, *J.C.S.*, 1927, 130, 1087). Many complex salts of Mo^{III}, *e.g.* K_3MoCl_6, are known. The sesquioxide Mo_2O_3 is doubtful, but the black **trihydroxide** $Mo(OH)_3$ is precipitated by alkali from the dark-coloured solution of molybdate reduced by zinc: it is sparingly soluble in acids and insoluble in alkalis. The **sesquisulphide** Mo_2S_3 is formed from MoS_2 at high temperatures.

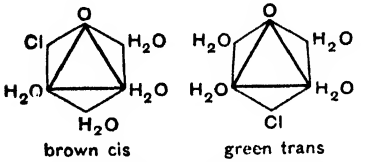
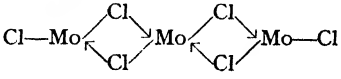
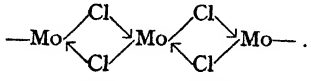


FIG. 308.—Isomers of $[MoOCl(H_2O)_4]$.

(5) *Compounds of* 2-*valent* Mo (Mo^{II}) are unimportant. The so-called **dichloride** $MoCl_2$ formed as an amorphous yellow solid residue on heating $MoCl_3$ in dry carbon dioxide: $2MoCl_3 = MoCl_2 + MoCl_4$, or by passing chlorine over molybdenum at 1200°, is really Mo_3Cl_6, probably with the structure:



It is insoluble in water but with hydrochloric acid it forms deep yellow needles of $H[Mo_3Cl_7(H_2O)],3H_2O$, and from solutions in alkali carbon dioxide precipitates $Mo_3Cl_4(OH)_2,8H_2O$, which dissolves in acids to form salts $[Mo_3Cl_4X_2]$, where X = Cl, Br, I, NO_3, $\frac{1}{2}SO_4$, probably containing the group



The red bromide Mo_3Br_6 reacts similarly to Mo_3Cl_6; it is diamagnetic (Tjabbes, 1932).

Molybdenum compounds are used in silk and wool dyeing, in colouring leather and rubber, and as a blue pigment for porcelain.

Tungsten

Tungsten as well as molybdenum was discovered by Scheele, who in 1781 obtained the yellow acidic trioxide WO_3 from the heavy Swedish mineral now called *scheelite*, calcium tungstate $CaWO_4$, but then called *tung sten* (= " heavy stone," s. g. 6·0). In 1783 the two brothers de Lhuyart discovered it in the mineral *wolframite*, ferrous tungstate, $FeWO_4$, s. g. 7·1 (p. 513), found in the United States, Bolivia, Portugal and Korea, but chiefly in Burma and China, and usually containing manganese $(Fe,Mn)WO_4$ (Balke, *Ind. Eng. Chem.*, 1929, **21**, 1002); they also first prepared metallic tungsten. *Tungstenite* WS_2 (cf. molybdenite MoS_2) is rare.

On boiling scheelite or wolframite with concentrated hydrochloric acid and adding some concentrated nitric acid, a yellow residue of WO_3 remains. This is purified by dissolving in ammonia, crystallising the ammonium tungstate, and heating this in air.

On sintering wolframite with sodium carbonate a soluble **sodium tungstate** is formed, which can be dissolved and crystallised as $Na_{10}W_{12}O_{41},28H_2O$, derived from **paratungstic acid** $H_{10}W_{12}O_{41}$ $(=12WO_3+5H_2O)$. The tendency to form complex polyacids is even more marked with tungsten than with molybdenum. Sodium tungstate is used as a mordant, etc. Cadmium tungstate $CdWO_4$ is used for fluorescent X-ray screens.

Acids precipitate from concentrated sodium tungstate solution in the cold white **α-tungstic acid** H_2WO_4,H_2O, somewhat soluble in water; from hot solutions yellow **β-tungstic acid** H_2WO_4, insoluble in water and all acids except HF, is precipitated. The α- and β-acids have distinct X-ray spectra (Morley, *J.C.S.*, 1930, 1987). Dialysis of a dilute solution of sodium tungstate acidified with hydrochloric acid gives **colloidal tungstic acid** (Graham, 1864), drying on evaporation to a gum-like solid, soluble in water. The molecular weight in solution corresponds with $(H_2WO_4)_7$ but, like the chromic acids (p. 748), it may be $H_2(WO_3)_xWO_4$.

On boiling a solution of sodium paratungstate $(Na_{10}W_{12}O_{41})$ with tungsten trioxide a solution is formed which deposits efflorescent crystals of **sodium metatungstate** (or **tetratungstate**) $Na_2W_4O_{13},10H_2O$: $Na_{10}W_{12}O_{41}+8WO_3=5Na_2W_4O_{13}$. Unlike the paratungstate this gives no precipitate with acid, as **metatungstic acid** $H_2W_4O_{13}$ $(=4WO_3+H_2O)$ is soluble; it is obtained in crystals $H_2W_4O_{13},8H_2O$ by decomposing BaW_4O_{13} with dilute sulphuric acid and evaporating the filtrate on a water bath and in a vacuum desiccator.

Metallic tungsten is obtained for use in making *tungsten steel* (a " high-speed " steel, 7–20 p.c. W, 2–6 p.c. Cr, 1 p.c. V, chisels of which can be used red-hot in lathe-turning) by reducing WO_3 with carbon in a crucible at a white heat: it is a grey powder, s. g. 19·3, m.p. 3390°, forming a hard white mass. Pure tungsten for lamp filaments is made by reducing pure WO_3 in dry hydrogen at 1200°, pressing the powder into rods, sintering these at 2500° in hydrogen, rolling and hammering at a very high temperature, and drawing (finally through bored diamonds) at 400°–650°. Sometimes a little ThO_2 is added to the WO_3 before reduction. The filaments are single crystals (Coolidge, *Ind. Eng. Chem.*, 1912, **4**, 2). Very pure tungsten is deposited by heating a tungsten wire at 1600°–1700° in WCl_6 vapour. Tungsten exists in two cubic forms, the common α-W and the β-W deposited electrolytically from a melt of WO_3 and a phosphate.

Tungsten is used in some very hard alloys: *kennametal* $(WTiC_2)$, *stellite* (Co, Cr, W), *widiametal* (WC_2 with 10 p.c. Co), etc., which are pressed from powders and sintered at a very high temperature.

The metal burns to WO_3 in oxygen at a red heat, and in chlorine to WCl_6 at 250°–300°. It does not combine with nitrogen at a red heat and is only slowly attacked by H_2SO_4, HCl and HF, but rapidly by fused alkali.

Tungsten shows valencies of 2, 3, 4, 5 and 6, the 6-valent compounds being most stable. Compounds of lower valencies are reducing agents. In concentrated hydrochloric acid, Cu, Bi and Bi amalgam reduce W^{VI} to W^{V}, and Pb, Cd, and amalgams of Pb, Zn and Cd to W^{III}, no W^{IV} being formed as an intermediate stage.

(1) *Compounds of 6-valent* $W(W^{VI})$. **Tungsten hexafluoride** WF_6 is a colourless fuming liquid, b.p. 19·5, almost gaseous at room temperature, formed by distilling WCl_6 with anhydrous HF, AsF_3 or SbF_5; it is hydrolysed by water to WO_3. The **oxyfluorides** WOF_4 and WO_2F_2 are known. The **hexachloride** WCl_6 (Wöhler, 1855) is formed in black crystals, m.p. 275°, b.p. 347°, by heating the metal in dry air-free chlorine. The vapour density is approximately normal at the b.p., but at higher temperatures dissociation into WCl_5 occurs. WCl_6 is insoluble in water. Two solid **oxychlorides** are known: red $WOCl_4$, obtained by passing WCl_6 vapour over heated WO_3: $2WCl_6 + WO_3 = 3WOCl_4$, and yellow WO_2Cl_2 formed by passing chlorine over heated WO_2 (Wöhler, 1823; Rose, 1837): $WO_2 + Cl_2 = WO_2Cl_2$. By heating WCl_6 in hydrogen or sometimes CO_2 at various temperatures the lower chlorides WCl_5 (Blomstrand, 1861), WCl_4 (Riche, 1856) and WCl_2 (Roscoe, 1872) are formed.

By adding K_2WO_4 to 30 p.c. hydrogen peroxide a yellow **pertungstate** K_2WO_8, $\frac{1}{2}H_2O$ crystallises, and there is also a crystalline Na_2WO_8,H_2O. These are salts of $W^{VI}O_4(O{\cdot}OH)_2$ containing 6-valent W (see H_2MoO_8, p. 753).

(2) *Compounds of 5-valent* $W(W^{V})$ are the **pentachloride** WCl_5; the blue **pentoxide** W_2O_5 formed by heating WO_3 and tungsten at 1000°; double chlorides of the **oxytrichloride** $W^{V}OCl_3$ (which is itself not known) $M^{I}_2WOCl_5$ and $M^{I}WOCl_4$, formed by reducing solutions of alkali tungstates with oxalic acid and tin and giving deep blue solutions in hydrochloric acid; **tungsticyanides** $M^{I}_3[W^{V}(CN)_8]$ forming yellow crystals and colourless solutions and obtained by oxidising the yellow tungstocyanides $M^{I}_4[W^{IV}(CN)_8]$ with $KMnO_4$ (Olsson, 1914); and *tungsten blue*, obtained by the partial reduction of WO_3 and probably a compound of WO_3 and W_2O_5, perhaps $(W^{V}O)_2(W^{VI}O_4)_3$.

(3) *Compounds of 4-valent* $W(W^{IV})$ are the **tetrachloride** WCl_4; the **dioxide** WO_2 formed as a brown powder by heating WO_3 in moist hydrogen at 900° or in red leaflets by the action of hydrochloric acid on a mixture of zinc and WO_3; the dark grey **disulphide** WS_2 formed from the elements; **tungstocyanides** $M^{I}_4[W^{IV}(CN)_8]$ formed by the action of MCN on the double oxychlorides of 5-valent W, $M^{I}_2WOCl_5$ and $M^{I}WOCl_4$ (see above); and the curious *tungsten bronzes* formed by heating acid tungstates in hydrogen or with zinc, or heating a tungstate with WO_3. The old formula for tungsten bronzes is $(M^{I}_2O)_x,(WO_3)_y,WO_2$, but all modern workers put $x = 1$ and formulate them as $M^{I}_2(W^{IV}O_3)_{y+1}$.

(4) *Compounds of 3-valent* $W(W^{III})$ are the greenish-yellow double salts of the trichloride WCl_3 (not itself known), $M^{I}_3W_3^{III}Cl_9$, obtained by reducing a solution of alkali tungstate in hydrochloric acid with tin, cooling and saturating with HCl gas (Olsson, 1913): they are strong reducing agents.

(5) *Compounds of 2-valent* $W(W^{II})$ are the **dichloride** WCl_2 and **di-iodide** WI_2, which, like the molybdenum compounds, are probably W_3Cl_6 and W_3I_6 (p. 754). Yellow crystals of $H[W_3^{II}Cl_7(H_2O)],3H_2O$ are formed from the dichloride and hydrochloric acid or by heating WCl_6 with aluminium, dissolving in hydrochloric acid and passing in HCl gas. It is less stable than the Mo compound.

Complex Acids

Molybdic and tungstic acids form complex **isopolyacids** such as $H_2Mo_4O_{13}$, $H_2Mo_6O_{25}$, $H_6Mo_7O_{24}$, $H_2W_4O_{13}$, $H_{10}W_{12}O_{41}$, and **heteropolyacids** with other acid radicals, such as the two *phosphomolybdic acids* $P_2O_5,24MoO_3,xH_2O$ and P_2O_5, $18MoO_3,xH_2O$; the two *phosphotungstic acids* $P_2O_5,24WO_3,xH_2O$ and P_2O_5, $18WO_3,xH_2O$ (others have been described); *borotungstic acid* $B_2O_3,24WO_3,xH_2O$ and its crystalline salts $5M_2O,B_2O_3,24WO_3,xH_2O$; *silicotungstic acids* SiO_2, $12WO_3,xH_2O$ and $SiO_2,10WO_3,xH_2O$ and salts; etc.

Phosphomolybdic acid $P_2O_5,24MoO_3,63H_2O$ is obtained in deep yellow octahedral crystals, m.p. 78°, by heating ammonium phosphomolybdate (p. 752) with aqua regia and recrystallising from water containing a little nitric acid. **Phosphotungstic acid** $P_2O_5,24WO_3,63H_2O$ is formed in colourless octahedral crystals by acidifying with sulphuric acid a solution containing 4 pts. of sodium tungstate and 1 of sodium phosphate, concentrating, extracting with ether, evaporating the ether solution and crystallising from water. It precipitates potassium and ammonium (but not sodium) salts, alkaloids and proteins.

Werner (1907), Miolati (1908) and Rosenheim (1911) formulated the complex acids as derived from simple acids by substitution of oxygen atoms by acid and polyacid radicals, *e.g.* $H_2W_4O_{13}$ from H_2WO_4 to form $H_2[WO(WO_4)_3]$. In some cases hypothetical acids of high basicity were assumed as being substituted, *e.g.* a phosphoric acid $H_7[PO_6] = (H_3PO_4 + 2H_2O)$ giving $H_7[P(Mo_2O_7)_6]$ as phosphomolybdic acid $\frac{1}{2}\{P_2O_5,24MoO_3,7H_2O\}$, and the existence of these was supposed to be confirmed by the conductivities and Ostwald's rule (p. 149). Jander, and Brintzinger (1925–36), from the rates of diffusion in solutions of varying pH, and conductimetric titrations (p. 110), claimed to have detected various complex ions of isopolyacids not in agreement with Rosenheim's theory; the heteropolyacids were regarded as molecular complexes, which is not in agreement with their great stability.

Pfeiffer (1918) suggested that MoO_3 and WO_3 *molecules* might be grouped round an octahedral XO_6 ion (X = P, As, etc.) in a second shell, *e.g.* $H_7[PO_6(WO_3)_{12}]$ instead of $H_7[P(W_2O_7)_6]$, and this idea was extended and modified on the basis of X-ray work (Pauling, *J.A.C.S.*, 1929, **51**, 1010, 2868; Riesenfeld and Tobiank, *Z. anorg. Chem.*, 1935, **221**, 287; Keggin, *Proc. Roy. Soc.*, 1934, **144**, 75; Santas, *ibid.*, 1935, **150**, 309; Bradley and Illingworth, *ibid.*, 1936, **157**, 113; Illingworth and Keggin, *J.C.S.*, 1935, 575).

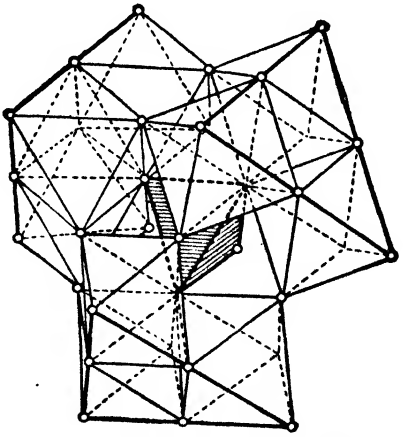


FIG. 309.—Structure of anion $XM_{12}O_{40}$.

Keggin's structure (Fig. 309), which can hardly be followed without a model, has a tetrahedral XO_4 ion (X = P, As, Si, B, etc.) at the centre, each of its four corners sharing oxygens with a group of three octahedra. Each octahedron has a Mo, W, etc., atom at the centre and shares oxygens with each of its two neighbours, forming *e.g.* the group $3Mo + 9O + 4O = Mo_3O_{13}$. The four groups so formed are linked by

sharing corners to form an anion $[XM_{12}O_{40}]^{n-8}$, where n is the charge on the central X ion. When these ions are packed in the crystal there are large gaps into which H_2O molecules can be packed.

Signer and Gross (1934) find this structure with the acids :

$H_4[SiW_{12}O_{40}]$ silicotungstic $\quad H_5[BW_{12}O_{40}]$ borotungstic $\quad H_6[H_2W_{12}O_{40}]$ metatungstic

and Illingworth and Keggin with :

$H_3[PMo_{12}O_{40}]$ phosphomolybdic $\quad H_3[AsMo_{12}O_{40}]$ arsenimolybdic $\quad H_4[SiMo_{12}O_{40}]$ silicomolybdic $\quad H_4[MnMo_{12}O_{40}]$ manganimolybdic

Uranium

The element uranium (named after the planet Uranus) was discovered in 1789 by Klaproth in *pitchblende* or *uraninite*, a heavy black mineral which is essentially U_3O_8 but contains iron, bismuth, lead, and sometimes thorium, rare earths, and zirconium. It always contains traces of radium (formed from the uranium, p. 198) ; *cleveite* and *bröggerite* are varieties richer in thorium and rare earths. Other minerals containing uranium are *carnotite* (p. 644) and *thorianite* (p. 534). Pitchblende occurs in Cornwall, Joachimsthal (Bohemia), Portugal, Katanga (Belgian Congo), the Caucasus and Canada (Great Bear Lake, the richest ore known). It is now used as a source of radium, the uranium being a by-product. The powdered ore is roasted and fused with sodium carbonate and nitrate, the mass boiled with water and the residue heated with diluted sulphuric acid with some nitric acid. The radium remains (as $RaSO_4$) in the residue. The solution is treated with excess of sodium carbonate, boiled, and the liquid containing **sodium uranyl carbonate** $Na_4[UO_2(CO_3)_3]$ neutralised with dilute sulphuric acid, when **sodium diuranate** $Na_2U_2O_7,6H_2O$ (*uranium yellow*) is precipitated. By using ammonium carbonate the soluble $(NH_4)_4[UO_2(CO_3)_3]$ is formed, which can be obtained in yellow crystals. On igniting these the black oxide U_3O_8 is formed, which dissolves in acids to form the **uranyl salts**, containing the bivalent radical $=UO_2$.

By heating U_3O_8 with charcoal or in hydrogen the black **dioxide** UO_2 is formed, which was regarded (even by Berzelius) as the metal : it is not reduced by hydrogen even at 2500°. On heating this in chlorine yellow crystalline **uranyl chloride** UO_2Cl_2 is formed, giving yellow complex chlorides $K_2[UO_2Cl_4]$, etc. This was thought to be uranium chloride until Peligot (1841) showed that when heated with carbon in a stream of chlorine, carbon monoxide is formed and **uranium tetrachloride** UCl_4 sublimes in dark green crystals ; on heating this with sodium he obtained metallic uranium.

The **metal** is difficult to prepare pure as it combines easily with oxygen, nitrogen and carbon. It is formed in white crystals (monoclinic ; Wilson, 1933) with a blue tinge by heating UCl_4 with sodium or calcium, or as a grey pyrophoric powder by the electrolysis of a melt of KUF_5 with NaCl and $CaCl_2$ at 775° with a molybdenum cathode (Driggs and Lilliendahl, *Ind. Eng. Chem.*, 1930, **22**, 516). The compact metal is silver-white, malleable and ductile, s. g. 18·7, and gives strong sparks when filed or when the powder is thrown into a flame. The powder oxidises in air and slowly decomposes water. On heating it burns in oxygen to U_3O_8 and in chlorine to UCl_4 ; it forms a yellow **nitride** $U_3^{IV}N_4$ at 1000°. An impure **carbide** UC_2 is formed from U_3O_8 and carbon in the electric furnace.

Uranium forms compounds in which it has valencies of 3, 4, 5 and 6, the U^{VI} compounds being most stable; U^{IV} compounds are green. The common compounds are **uranyl salts**, UO_2X_2, derived from $=U^{VI}O_2$.

The **fluorides** UF_4 (green insoluble amorphous powder, stable to heat) and UF_6 (white soluble monoclinic crystals, sublimes at 56°) are formed by the reactions: $2UCl_5 + 5F_2 = UF_4 + UF_6 + 5Cl_2$ and $2UCl_5 + 10HF = UF_4 + UF_6 + 10HCl$ (Ruff, 1911). The action of water on UF_6 gives yellow **uranyl fluoride** UO_2F_2, which forms $K_3[UO_2F_5]$. A solution of UO_2F_2 and green insoluble **uranous oxyfluoride** $U^{IV}OF_2$ is formed by the action of hydrofluoric acid on U_3O_8:

$$U_3O_8 + 6HF = UOF_2 + 2UO_2F_2 + 3H_2O,$$

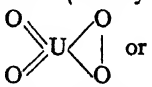
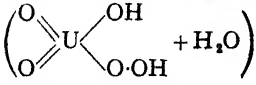
and UOF_2 by electrolysing a solution of UO_2Cl_2 in HCl and HF.

There are three chlorides, UCl_3, UCl_4 and UCl_5. The **tetrachloride** UCl_4 sublimes in dark green octahedral crystals, b.p. 618°, soluble in water, alcohol and benzene, on heating a mixture of UO_2 or U_3O_8 and carbon in chlorine, a little UCl_5 being formed. The **pentachloride** UCl_5 (which may be $Cl_4U^{IV}\begin{smallmatrix}Cl\\ \diagup\ \diagdown\\ Cl\end{smallmatrix}U^{VI}Cl_4$, as it is otherwise the only compound of U^{V}) is formed in ruby-red crystals or a brown powder by the action of chlorine on UCl_4. The **trichloride** UCl_3 is formed in red needles by heating UCl_4 in hydrogen and a red solution by reducing a solution of UCl_4 in hydrochloric acid with zinc: it is a strong reducing agent. UBr_3, UBr_4, UO_2Br_2 and complex salts $M_3[UBr_6]$ and $M_2[UO_2Br_4]$, and UI_4 and UO_2I_2 are known.

The **oxides** are UO_2, U_3O_8, U_2O_5 (?) and UO_3. The **dioxide** $U^{IV}O_2$, black octahedral crystals with a fluorite lattice (p. 242), is formed by strongly heating U_3O_8 in hydrogen. It dissolves in acids to form the yellow uranyl salts, but is sparingly soluble except in nitric acid.

Uranyl nitrate $UO_2(NO_3)_2,6H_2O$ forms yellow deliquescent rhombic crystals with a green fluorescence, soluble in water and ether; **uranyl acetate** $UO_2(C_2H_3O_2)_2,2H_2O$ forms similar crystals. **Uranyl hydrogen phosphate** $UO_2HPO_4,4H_2O$ is yellow and sparingly soluble; **uranyl ammonium phosphate** $UO_2NH_4PO_4$ is formed as a greenish-yellow precipitate with ammonium phosphate. **Uranyl sulphate** $UO_2SO_4,3H_2O$ and $UO_2SO_4,\frac{7}{2}H_2O$, and other salts are known, also **uranyl sulphide** UO_2S. **Uranium sulphate** $U^{IV}(SO_4)_2$ is known in a large number of green crystal hydrates and double salts, *e.g.* green $K_2U(SO_4)_3,2H_2O$. Uranium salts are very poisonous.

The oxide U_3O_8 may be $U^{IV}(U^{VI}O_4)_2$. The **pentoxide** U_2O_5, said (Schwarz, 1920) to be formed on heating U_3O_8 in CO_2 at 1122°, is somewhat doubtful (Biltz, 1927). The orange-coloured amorphous **trioxide** UO_3, possibly $(U^{VI}O_2)O$, is formed by heating $UO_2(NO_3)_2$ at 250° or (pure) by heating the peroxide UO_4 in oxygen (Biltz, 1927; Hüttig and Schroeder, 1922). It forms hydrates with 2, 1 and $\frac{1}{2}H_2O$, the *uranic acids* H_2UO_4, H_2UO_4,H_2O (cf. Mo and W) and $H_2U_2O_7$. The trioxide is amphoteric, dissolving in acids to form uranyl salts: $UO_3 + 2H^{\cdot} = UO_2^{\cdot\cdot} + H_2O$, and with alkalis forming **uranates**, which are precipitated by alkalis from uranyl salt solutions: $UO_2^{\cdot\cdot} + 4OH' = UO_4'' + 2H_2O$. The alkali uranates are usually formulated $K_2U_2O_7,3H_2O$ and $Na_2U_2O_7,6H_2O$ (*uranium yellow*, used for painting porcelain and making yellow fluorescent glass), but the formula is said (Tilk and Klemm, 1929) to be $K_2U_7O_{22}(=K_2UO_4 + 6UO_3)$, or with excess of alkali $K_4U_6O_{17}(=2K_2UO_4 + 3UO_3)$.

A yellowish-white **uranium peroxide** $UO_4,3H_2O$, or $UO_4,2H_2O$ when dried at 100°, is precipitated by hydrogen peroxide from a uranyl salt solution (Fairley 1877): $UO_2^{\cdot\cdot} + H_2O_2 = UO_4 + 2H^{\cdot}$. Its structure is probably  or  . A red colour due to a **peruranate** is formed in presence of alkali: it seems to contain *e.g.* $(KO)_4U$  $,6H_2O_2,xH_2O$, with more active oxygen than corresponds with UO_4 (Schwarz and Heinrich, 1935).

A solution of zinc uranyl acetate is a reagent for sodium. A mixture of 100 g. of uranyl acetate $UO_2(C_2H_3O_2)_2,2H_2O$ and 60 c.c. of acetic acid is made up to 500 c.c. A mixture of 300 g. of zinc acetate $Zn(C_2H_3O_2)_2,2H_2O$ and 60 c.c. of acetic acid is made up to 500 c.c. The two solutions are mixed, and the solution after one or two days is filtered. It gives a yellow precipitate of $NaZn_2(UO_2)_2(C_2H_3O_2)_9$, after potassium salts have been removed by precipitation with zinc perchlorate.

When uranium is bombarded with neutrons, fission of the nucleus occurs, with the formation of fragments of about equal masses and the liberation of a large amount of energy owing to the loss of total mass in the process (p. 208). Free neutrons are also formed, so that a type of chain reaction (p. 784) is possible. The isotope of uranium ^{235}U is particularly liable to undergo fission with bombarding neutrons of low energy, and with a sufficiently large mass of uranium, a violent explosion, liberating an immense amount of energy, may occur. This may be caused by bringing together two pieces of uranium below the critical size, in presence of a neutron source, and this is the principle of the "atomic bomb". Neutrons of the proper energy are absorbed by the nucleus of ^{238}U (atomic number 92), forming a nucleus of mass 239, which emits two electrons in succession to form elements of atomic numbers 93 and 94, which are "trans-uranic elements" not found in nature.

CHAPTER XXVII

GROUP VII: FLUORINE AND CHLORINE

GROUP VII consists of two sub-groups of widely divergent character. The (*b*) sub-group comprises the elements fluorine, chlorine, bromine and iodine, with closely related chemical properties, forming a group long known as the *halogens* (Greek *hals*, sea-salt). Fluorine and its compounds show divergences from the other halogens, as is common with the first members of other groups in the periodic system, and fluorine has been called a "super-halogen." The gradation of *physical properties* of the halogens and their hydrides is seen in the following table:

	F_2	Cl_2	Br_2	I_2	HF [1]	HCl	HBr	HI
Atomic number	9	17	35	53				
Electron configuration	2·7	2·8·7	2·8·18·7	2·8·18·18·7				
State at 15°	gas	gas	liquid	solid	liquid	gas	gas	gas
Colour	pale yellow	greenish yellow	dark red	black (vapour violet)	All colourless			
M.p.	−217·8°	−101·6°	−7·2°	113·9°	−83°	−111·4°	−86·9°	−50·8°
B.p.	−187°	−34·6°	58·7°	184·4°	19·4°	−85·0°	−66·7°	−35·4°
Normal density of gas	1·70	3·212	—	—	—	1·63915	3·644	5·78882
Density of liquid at b.p.	1·108	1·557	2·948	3·706	0·98	1·181	2·160	2·80
Critical temperature	−129°	144°	311°	553°	230·2°	51·45°	89·8°	150°
Critical pressure (atm.)	55	76·1	102	—	—	81·52	84·4	80·8
Solubility g./lit. at 0° (HX in 1 kg. H_2O)	decomp.	14·6	41·5	0·162	∞	823	2212	2483 [2]
Heat of formation, k. cal.	—	—	—	—	64·5	22	12·1 [3]	−6·1 [4]
Energy of formation from atoms, k. cal.	—	57	46	36	140	102	86	66
Atomic distance in A.	1·45	1·98	2·22	2·56	0·864	1·28	1·42	1·6

[1] The properties of hydrofluoric acid are abnormal (see p. 769). [2] At 10° (425 vols. in 1 vol. H_2O).
[3] From liquid Br_2. [4] From solid I_2; from gaseous I_2, +4·5 k. cal.

The crystal structures of the solid hydracids from X-ray and electron diffraction measurements are: HF, long zig-zag chains with 4 molecules per unit cell (Holm and Strunz, *Z. phys. Chem.*, 1939, **43B**, 229; Bauer, Beach and Simons, *J.A.C.S.*, 1939, **61**, 19); HCl, cubic (Simon and Simson, *Z. Phys.*, 1924, **21**, 168); HBr, face-centred cubic (Natta, *Gazz.*, 1933, **63**, 425); HI, tetragonal face-centred (Ruhemann and Simon, *Z. phys. Chem.*, 1931, **15B**, 389).

The stability both of X_2 and HX decreases from F to I. The F_2 molecule is very stable, Cl_2 is only slightly dissociated above 1100°, Br_2 about 6 p.c., and I_2 quite extensively below 1000°. The molecules HX behave similarly; HF and HCl are very stable, HBr is only about 1 p.c. dissociated even at 1200°, HI about 20 p.c. at 400°. These results are in agreement with the heats of formation of X_2 and HX.

The decreasing affinity of halogens for *hydrogen* is shown by the fall in heat of reaction from fluorine to iodine. Hydrogen combines explosively with fluorine in the dark, explosively with chlorine on exposure to light, non-explosively with bromine and iodine on heating in presence of platinum, the reactions being reversible and with iodine incomplete. The stability of the *oxygen compounds* is anomalous: F_2O is stable, the oxides of chlorine are explosive,

those of bromine are less stable than those of chlorine, those of iodine are fairly stable. A list of the oxygen compounds of the halogens is given below.

F_2O colourless gas, m.p. $-223{\cdot}8°$, b.p. $-146{\cdot}5°$. Cl_2O, brownish-yellow gas, m.p. $-120{\cdot}6°$, b.p. $+2{\cdot}0°$. Br_2O, brownish gas?	F_2O_2 orange-red solid, m.p. $-163{\cdot}5°$, decomp. above $-100°$ into F_2 and O_2.	ClO_2 orange-yellow gas, m.p. $-59°$, b.p. $11{\cdot}0°$. s. g. liquid 1·66 at 0°. BrO_2 yellow solid, decomp. at 0°. IO_2 yellow solid, decomp. at 130° into I_2O_5 and I_2.	I_4O_9 pale yellow solid, decomp. at 75° into I_2O_5, I_2 and O_2.	Br_2O_2 white solid, stable at $-80°$.	
I_2O_5 white solid, m.p. decomp. 300°, s. g. 4·98.	Cl_2O_6 dark red liquid, m.p. 3·5.	Cl_2O_7 colourless liquid, m.p. $-91{\cdot}5°$, b.p. 82°.			

The *oxyacids* are generally more stable the more oxygen they contain: none are definitely known for fluorine, the others generally increase in stability from chlorine to iodine; perchloric, iodic, and the periodic acids are known in the pure state, but the others only in solution or as salts. The common periodic acid has the unusual formula H_5IO_6 and the tendency of the halogen to assume an octahedral arrangement of 6 oxygens is also found in solid iodic acid.

HOCl aq.	HOBr aq.	HOI aq.
$HClO_2$ aq.	$HBrO_2$ (salts)	HIO_2 aq.
$HClO_3$ aq.	$HBrO_3$ aq.	HIO_3
$HClO_4$ and hydrates		HIO_4, $H_4I_2O_9$, H_5IO_6

All the halogens react to some extent with *water*: with fluorine the reaction is energetic and anomalous (p. 766); the remaining halogens are *hydrolysed* according to the reaction

$$X_2 + H_2O \rightleftharpoons HOX + H^{\cdot} + X'$$

decreasing in extent from Cl_2 to I_2 (which scarcely reacts), the hydrolysis constants at 25° $K_h = [HOX][H^{\cdot}][X']/[X_2]$ being: Cl_2 $4{\cdot}5 \times 10^{-4}$, Br_2 $5{\cdot}2 \times 10^{-9}$, I_2 3×10^{-13}. With *alkali* the reactions proceed further and in presence of excess of alkali the *hypohalite ion* OX' is stable, except OI':

$$X_2 + 2OH' = OX' + X' + H_2O,$$

but in presence of excess of halogen the *halate* XO_3' and halide X' ions are formed (p. 793). With chlorine and bromine crystalline *hydrates* $Cl_2,6H_2O$ and $Br_2,10H_2O$ are formed.

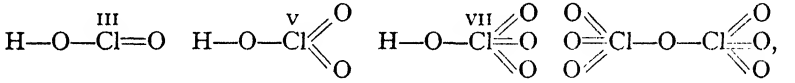
The halogens form compounds with one another (p. 815):

ClF colourless gas, m.p. $-161°$, b.p. $-103°$.	ClF_3 colourless gas, m.p. $-83°$, b.p. $11{\cdot}3°$.	BrF_5 colourless liquid, m.p. $-61{\cdot}3°$, b.p. $40{\cdot}5°$.	IF_7 colourless gas, m.p. $5{\cdot}5°$, subl. $4{\cdot}5°$.
BrF reddish-brown liquid, m.p. $-33°$, b.p. 20°.	BrF_3 colourless liquid, m.p. $-2°$, b.p. 127°.	IF_5 colourless liquid, m.p. 8°, b.p. 97°.	
BrCl unstable.	ICl_3 yellow rhombic crystals, m.p. (decomp.) 67°, or 101° in Cl_2 at 16 atm.		
ICl 2 dark red solid forms: rhombic, m.p. $13{\cdot}92°$; cubic, m.p. $27{\cdot}2°$; b.p. $97{\cdot}4°$.			
IBr black solid, m.p. 36°, b.p. 116°.			

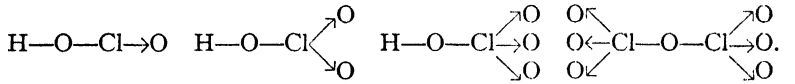
Halogens displace one another from halides: $X_2 + 2Y' = 2X' + Y_2$ in the order F, Cl, Br, I, but from oxygen compounds iodine displaces chlorine: $2KClO_3 + I_2 = 2KIO_3 + Cl_2$. The halogens combine with sulphur (except iodine), phosphorus, arsenic and many metals, the reactions being often attended by incandescence: the vigour of the reaction decreases from fluorine to iodine.

The *structural formulae of the oxides and oxyacids of the halogens* are still rather uncertain. It is accepted that, except in the monoxides X—O—X and hypo-halogen acids H—O—X, the halogens have higher valencies. Chlorine dioxide has an odd electron and is paramagnetic: it may be represented by the formula $:\ddot{O}::\ddot{Cl}:\ddot{O}:$ or as a resonance hybrid with a 3-electron bond, $:\ddot{O}:Cl:\ddot{O}: \quad :\ddot{O}:Cl:\ddot{O}:$

The formulae proposed by Blomstrand (1869):



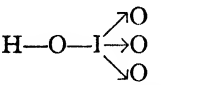
were generally replaced by formulae with coordinate links:



The Cl to O distance in the ClO_3' and ClO_4' ions in crystals, 1·48 A. (Dickinson and Goodhue, *J.A.C.S.*, 1921, **43**, 2045) and that for the chlorite ion (1·59 A.; Levi and Scherillo, 1930) show, however, that there is a large amount of double bond character, but the bond angles are close to those expected for single covalent bonds (Pauling, *The Nature of the Chemical Bond*, 1940, 245).

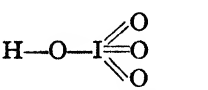
The formulae of the bromine and iodine compounds are usually written, by analogy, in the same way of those of chlorine. Iodic acid crystals are aggregates of HIO_3 molecules held together by bifurcating hydrogen bonds, resulting in IO_6 octahedra with three strong and three weak bonds (Rogers and Helmholz, *J.A.C.S.*, 1941, **63**, 273).

The three known periodic acids HIO_4, $H_4I_2O_9$, and H_5IO_6 all contain 7-valent iodine and are often written with coordinate links



$O{\leftarrow}I(OH)_5$, etc.

According to Pauling (*The Nature of the Chemical Bond*, 1940, 246) the bond distance 1·93 A. in IO_6^{5-} shows that the links have some double bond character:



$O{=}I(OH)_5$, etc.

but this is less than in the tetrahedral ions SO_4'', etc. (p. 715).

The crystals of H_5IO_6 show no water bands in the infra-red spectrum and the IO_6 ion is shown by X-rays to be octahedral, so that the acid is not $HIO_4,2H_2O$. The salt $Na_2H_3IO_6$ does not lose water in vacuum at 100°, but $Ag_2H_3IO_6$ does and may be $Ag_4I_2O_9,3H_2O$ (Partington and Bahl, *J.C.S.*, 1934, 1091). The X-ray spectrum shows that $(NH_4)_2H_3IO_6$ contains the IO_6 ion (Helmholz, *J.A.C.S.*, 1937, **59**, 2036).

All the halogens form complex acids with other elements and these or their salts are particularly stable in the case of fluorine, *e.g.* KBF_4, K_2SiF_6.

Fluorine

Calcium fluoride CaF_2 occurs as the mineral *fluorspar* or *fluorite* in many places, *e.g.* in England in Derbyshire (where the ornamental blue or purple forms are called " blue john ") and Weardale, and in Illinois and Kentucky in the U.S.A. It occurs in cubes with an octahedral cleavage and also in compact masses like marble. The colourless crystals show a bluish *fluorescence* (so named after fluorspar). Blue, green, and (rarely) pink varieties are found. All kinds show a green phosphorescence when heated.

The blue colour is sometimes due to organic matter and disappears on heating (Blount and Sequeira, *J.C.S.*, 1919, **115**, 705). Colourless forms become blue when exposed to radium emanation. Some varieties of fluorspar (*e.g.* of Wölsenberg) contain free fluorine (Henrich, 1920).

Cryolite (Greek *kryos*, ice, *lithos*, stone) Na_3AlF_6 occurs in Greenland, and *fluorapatite* $CaF_2,3Ca_3(PO_4)_2$ (p. 376) is common. Fluorides occur in *topaz* $Al_2SiO_4(F,OH)_2$, in *tourmaline* (aluminium borosilicate) and in some calcium phosphate deposits, notably Algerian. Small quantities of calcium fluoride in soil (probably from apatite) are absorbed by plants, the ash of which contains about 0·1 p.c. of fluorine ; beech leaves contain 0·1 p.c. Bones and teeth contain fluorides, perhaps as apatite, notably teeth enamel (0·1–0·2 p.c. F ; 0·3 p.c. in dog's) and fossil bones (0·88–6·2 p.c. CaF_2). Traces of fluorine compounds occur in volcanic gases.

Drinking water containing 2 mg. per lit. of F as fluoride causes " mottled teeth " ; a safe upper limit is given as 1·7 mg. per lit. New Maldon (Essex) water contains 5 mg. per lit., and some mineral waters (*e.g.* of Gerez, Portugal) contain more. The fluoride content is reduced by precipitation with aluminium sulphate or filtration through activated alumina.

Fluorspar (native calcium fluoride CaF_2) was described, as *fluor* (from Latin *fluo*, I flow, as it melts at a red heat, and is used as a flux), by Agricola in 1530. Its composition was for long unknown. Crude hydrofluoric acid seems to have been obtained about 1720 (Partington, *Manch. Mem.*, 1923, **67**, No. 6, 73). Scheele in 1771 showed that fluorspar is the lime salt of a peculiar acid which he obtained impure by distilling fluorspar with concentrated sulphuric acid in a glass retort, which was corroded, and a gas was formed (SiF_4) depositing gelatinous silica when passed into water. J. C. F. Meyer (1781) and Wenzel (1783) used iron and lead vessels (suggested by Wiegleb in 1781), respectively, and obtained fairly pure hydrofluoric acid solution and some salts, and also explained the action on glass. Scheele (1786) used a tin retort. Gay-Lussac and Thenard

(1809) obtained very concentrated hydrofluoric acid, which they regarded as the oxide of an unknown radical, but Ampère in 1810 suggested that it was a compound of hydrogen and an element fluorine, which was first isolated by Moissan in 1886 (see Moissan, *Le Fluor*, Paris, 1900).

The isolation of fluorine.—The isolation of fluorine was long one of the master problems of inorganic chemistry. The attempts of Davy, Fremy, Nicklès, Louyet, and Gore towards its solution were unsuccessful. With platinum vessels, a chocolate-coloured powder of PtF_4 was obtained ; carbon vessels were attacked with the formation of gaseous CF_4. Attempts to electrolyse hydrofluoric acid met with no success ; the aqueous acid gave only ozonised oxygen and hydrogen, the anhydrous acid is a non-conductor.

Moissan in 1886 found that the anhydrous acid conducts when potassium hydrogen fluoride KHF_2 is dissolved in it. The solution was electrolysed in a U-tube of platinum-iridium alloy with electrodes of the same metal, the whole being strongly cooled. Hydrogen was evolved from the cathode and fluorine from the anode. In 1899 Moissan used a copper apparatus (which apparently becomes coated with a protecting film of fluoride), retaining platinum-iridium for the electrodes.

A U-tube (Fig. 310) of 300 c.c. capacity contains 60 g. of acid potassium fluoride dissolved in 200 c.c. of anhydrous hydrofluoric acid. The electrodes

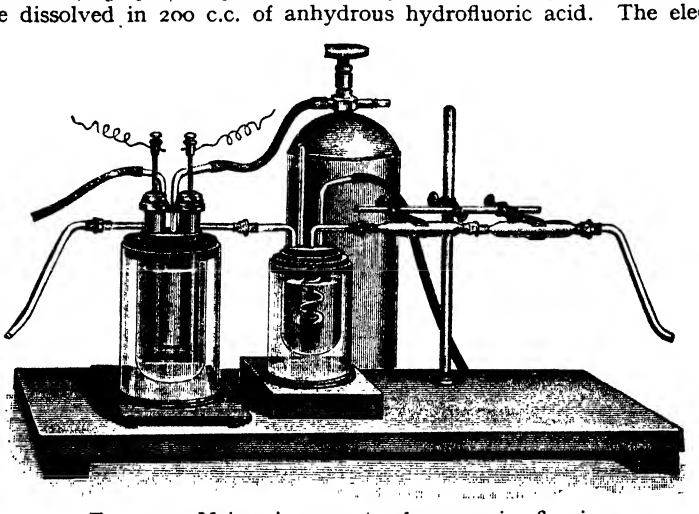


FIG. 310.—Moissan's apparatus for preparing fluorine.

are insulated by stoppers of fluorspar covered outside with shellac. The tube is immersed in a bath of methyl chloride b.p. $-23°$, constantly renewed, and a potential of 50 volts applied. The fluorine evolved from the anode at the rate of about 5 lit. per hour passed through a platinum or copper spiral cooled in methyl chloride, and a tube of the same metal packed with fused sodium fluoride, to remove hydrofluoric acid. By collecting and measuring the hydrogen from the cathode by upward displacement in two inverted flasks in series filled with

carbon dioxide, and absorbing the fluorine in iron wire in a weighed platinum tube, Moissan found that for every g. of hydrogen evolved the iron increased in weight by 19 g. The gas was therefore free fluorine. The electrolyte is probably potassium fluoride, the acid acting as an ionising solvent.

Fluorine is prepared by the electrolysis of fused $NaHF_2$ or better KHF_2. The pure and dry KHF_2 (m.p. 217°) is fused in an electrically heated copper apparatus, with graphite electrodes.

One form of apparatus (Fig. 311) consists of an electrically heated copper V-tube *AA* with electrodes *RR* of Acheson graphite rods insulated in bakelite cement stoppers *BB*. A current of 5 amp. at 12 volts is used. The fluorine (0·92 lit. per hour) is purified by passing through two copper U-tubes *F* and *G* containing dry sodium fluoride (Dennis, Veeder and Rochow, *J.A.C.S.*, 1931, **53**, 3263; cf. Schumb and Gamble, *ibid.*, 1930, **52**, 4302; Denbigh and Whytlaw-Gray, *J. S. C. I.*, 1934, **53**, 139 T.; Damiens, *Bull. Soc. Chim.*, 1936, **3**, 1; Emeléus, *J.C.S.*, 1942, 441).

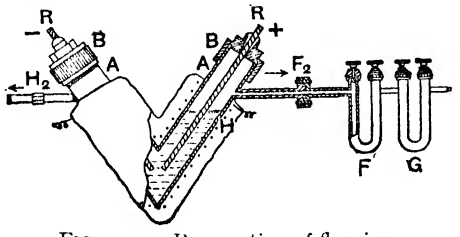


FIG. 311.—Preparation of fluorine.

Small quantities of fluorine are evolved on heating potassium fluorplumbate, made by the action of hydrofluoric acid on potassium plumbate; at 230°–250° this loses hydrofluoric acid and at higher temperature evolves free fluorine (Brauner, 1894):

$$PbF_4,3KF,HF = HF + K_3PbF_7\,; \quad K_3PbF_7 = K_3PbF_5 + F_2.$$

Cobaltic fluoride CoF_3 evolves fluorine on heating.

Properties of fluorine.—Fluorine is a *pale* greenish-yellow gas with very little action on glass below 100°, and may be kept in dry glass vessels. It has a powerful smell like that of hypochlorous acid, but is not so poisonous as hydrofluoric acid vapour. By weighing in a glass flask Moissan (1904) found the density 18·91 (H = 1), corresponding with F_2. Liquid fluorine was obtained by Moissan and Dewar (1897) by cooling in liquid oxygen boiling in vacuum; it is clear yellow. Solid fluorine was obtained by Dewar (1903) by cooling in liquid hydrogen; it is pale yellow, colourless at −252°.

Fluorine fumes in moist air, forming hydrofluoric acid and oxygen. Moissan (1899) found that water dropped into fluorine evolves strongly ozonised oxygen, the gas becoming blue, but Lebeau and Damiens (1927–29) with pure fluorine obtained only oxygen and hydrogen peroxide, slowly with dilute fluorine.

Fluorine is the most active element known, but it does not combine directly with oxygen or nitrogen, although compounds with these are formed indirectly.

A jet of fluorine inflames in a jar of hydrogen, burning with a red-bordered flame to form hydrogen fluoride. Moissan and Dewar found that solid fluorine explodes in contact with liquid hydrogen at −252°, and Moissan that moist gaseous fluorine and hydrogen explode in the dark. Others say the dry gases

do not react at room temperature, but the results are divergent (Aoyama and Kanda, 1937 ; Bodenstein, 1937).

Fluorine combines with chlorine only on heating, forming ClF and ClF_3 ; bromine burns to BrF_3, and iodine to IF_5. A mixture of fluorine and oxygen explodes by the action of the silent discharge. Sulphur, selenium and tellurium burn to gaseous SF_6 (with some S_2F_{10}), SeF_6 and TeF_6, phosphorus to PF_3 and PF_5, and arsenic to AsF_3 and AsF_5. Boron and silicon burn to BF_3 and SiF_4 (liquid fluorine does not attack silicon) ; finely divided carbon burns to CF_4 and other carbon fluorides, graphite reacts at a dull red heat, but diamond not at all. Alcohol, ether and turpentine inflame.

Sodium, potassium, calcium, magnesium powder and antimony inflame in fluorine ; massive magnesium, silver, zinc, aluminium, chromium, tin, lead and nickel react with incandescence on heating. Silver, copper and lead are only slowly attacked in the cold ; copper and gold are attacked at a red heat, but bismuth hardly even then. Mercury becomes covered with a pellicle of fluoride and fluorine can be kept over mercury for some time. The metals not attacked at the ordinary temperature form a protective coating of fluoride. Osmium burns above 250°, platinum is strongly attacked at 500°-600° (especially in presence of HF), whilst palladium, ruthenium and iridium are attacked only at a red heat.

Phosphorus pentoxide is not attacked at the ordinary temperature but on heating it burns to PF_3 and POF_3. Dry silica becomes incandescent in the gas but does not react with liquid fluorine. Hydrogen chloride reacts with flame and sometimes with explosion : $2HCl + F_2 = 2HF + Cl_2$; hydrogen bromide and iodide form HF and bromine and iodine fluorides ; hydrogen sulphide burns, forming SF_6 and HF ; ammonia is decomposed. Sodium chloride reacts in the cold : $2NaCl + F_2 = 2NaF + Cl_2$, potassium bromide and iodide with flame to form KF and BrF_3 or IF_5 ; phosphates form fluorides and POF_3.

Fluorine is an active oxidising agent, converting chromic salts into chromic acid, potassium sulphate to persulphate and iodate to periodate. Fluorides promote many electrolytic oxidations, *e.g.* of phosphates to perphosphates (p. 611).

Hydrofluoric Acid

Hydrogen and fluorine combine with explosion to form hydrofluoric acid HF. This is usually prepared by heating a fluoride (*e.g.* calcium fluoride, or cryolite Na_3AlF_6) with concentrated sulphuric acid, or by heating an alkali acid fluoride such as KHF_2, and condensing the acid, b.p. 19·4°, in a freezing mixture :

$$CaF_2 + H_2SO_4 = CaSO_4 + 2HF$$
$$KHF_2 = KF + HF.$$

Most fluorspar contains silica, giving acid contaminated with H_2SiF_6 ; this is not the case with cryolite.

Powdered fluorspar free from silica is distilled with 90 p.c. sulphuric acid in a cast-iron retort ; if more concentrated sulphuric acid is used fluosulphonic

acid is formed, p. 717). The hydrofluoric acid vapour is condensed in a strongly cooled steel, copper or lead receiver. The acid is purified by fractionation in steel apparatus, and is nearly anhydrous (0·1–0·2 p.c. H_2O, 0·01–0·1 p.c. SiF_4, and a trace of SO_2); it is stored in steel cylinders or tanks (Simons, *Ind. Eng. Chem.*, 1940, **32**, 178). If the lead receiver contains water the aqueous acid (40 p.c. HF, s. g. 1·13) is obtained; this may be kept in a gutta-percha bottle, but more concentrated acid, which attacks gutta-percha, is kept in ceresin wax bottles. The anhydrous acid is kept in well-closed platinum, gold or silver vessels.

Anhydrous hydrofluoric acid was prepared by Fremy in 1856 by heating dry potassium hydrogen fluoride in a platinum retort with a condenser of the same metal: $KHF_2 = KF + HF$. Copper apparatus may also be used. The liquid is collected in a platinum or copper flask cooled in a freezing mixture.

The KHF_2 crystallises on adding potassium carbonate to pure hydrofluoric acid solution in a silver dish. It is first dried at 100°, and then exposed in a vacuum desiccator over concentrated sulphuric acid and caustic potash, powdering from time to time. It melts at 230° and decomposes at higher temperature (Fredenhagen and Cadenbach, *Z. anorg. Chem.*, 1929, **178**, 289). Traces of moisture are removed from hydrofluoric acid by electrolysis with platinum electrodes; when all the water is removed the acid becomes non-conducting.

Anhydrous hydrofluoric acid is a colourless strongly-fuming liquid, s. g. 1·0 at 0°, 0·988 at 15°. It does not solidify till cooled at −102°, but the colourless transparent solid melts at −83°. When quite dry the liquid acid does not attack metals at room temperature, except potassium, which explodes. Moissan says the dry *gas* attacks glass but not the dry *liquid*, whilst Gore says just the opposite. In presence of traces of water the liquid attacks glass violently and dissolves most metals with evolution of hydrogen.

Commercial hydrofluoric acid (40–60 p.c.) is used in making artificial cryolite (p. 423), in etching glass, and removing sand from castings and silica from canes.

The alkali metals and calcium in the glass form fluorides; with gaseous or concentrated hydrofluoric acid the silicon forms silicon fluoride, with the solution hydrofluosilicic acid is formed. Etchings with the solution are clear, those with the gas or a solution containing ammonium fluoride are opaque.

Zinc and sodium fluorides are used in preserving wood, sodium fluoride as an insecticide and in killing "wild yeasts" which form fusel oil in fermentation, the normal yeast cells being capable of becoming accustomed to it.

Hydrofluoric acid and its vapour are dangerous corrosive poisons; they attack the skin violently, forming sores which heal with great difficulty, and rubber gloves should be used in working with the acid.

Hydrofluoric acid forms a solution of maximum b.p. (120°, 36 p.c. HF). The freezing-point curve has three maxima corresponding with crystal *hydrates* HF,H_2O (m.p. −35·4°), $2HF,H_2O$ (m.p. −75·2°) and $4HF,H_2O$ (m.p. −100·3°) (Cady and Hildebrand, *J.A.C.S.*, 1930, **52**, 3843). The heat of neutralisation is abnormally high, 16,270 g. cal. instead of 13,700 g. cal., as it is a fairly weak

acid and evolves heat on ionisation. In 0·1 *N* solution it is only 15 p.c. ionised. If excess of acid is added to the neutral salt solution 330 g. cal. are absorbed per mol of salt.

The *formula of hydrofluoric acid* was determined by Gore (1869), who heated silver fluoride in hydrogen in a platinum vessel and obtained twice the volume of hydrogen fluoride at 100°, hence the formula is HF : $2AgF + H_2 = 2Ag + 2HF$. Mallet (1881) determined the vapour density at 30·5° in a glass flask coated inside with paraffin wax and found 19·66 (H = 1), corresponding with H_2F_2. Thorpe and Hambly (*J.C.S.*, 1889, **55**, 163) determined the vapour density at various temperatures and pressures in a platinum flask, and found that the density varies considerably with temperature and pressure. At 88° and 741 mm. the density corresponds with HF ; at lower temperatures it approximated to the value for H_3F_3 and no indication of the existence of H_2F_2 was found, the density falling continuously with rise of temperature or decrease of pressure to the value for HF.

Simons and Hildebrand (*J.A.C.S.*, 1924, **46**, 2183) concluded from vapour pressure and density measurements that the gas is a mixture of HF and H_6F_6 molecules in equilibrium at 15°–19°, but Thorpe and Hambly's results were confirmed by Fredenhagen (1934).

Transport numbers in concentrated solutions indicate the existence of the ion HF_2' (Hudleston, etc., *J.C.S.*, 1924, **125**, 260 ; 1925, **127**, 1122). The ion has a linear structure F—H—F′ in solid KHF_2, the F to F distance being 2·24 A. (Bozorth, *J.A.C.S.*, 1923, **45**, 2128). In liquid hydrofluoric acid the HF molecules are probably associated by hydrogen bonds.

The **fluorides** differ in many ways from the other halides. Silver fluoride is very soluble, calcium fluoride nearly insoluble, in water. Cryolite Na_3AlF_6 and the corresponding ferric compound Na_3FeF_6 are insoluble. If a ferric salt is added to sodium fluoride solution Na_3FeF_6 is precipitated, and a fluoride may be titrated in this way, excess of ferric salt giving a red colour with thiocyanate. Fluorine differs from the other halogens in forming many *very stable* complex acids, *e.g.* HBF_4 and H_2SiF_6, and complex salts, *e.g.* K_2TiF_6 and K_2NbOF_5.

Fluorine oxides.—Although fluorine and oxygen do not combine directly on heating, two oxides of fluorine (or fluorides of oxygen) F_2O and F_2O_2 are known.

Fluorine monoxide F_2O was obtained by Lebeau and Damiens in 1927 by passing fluorine at the rate of 1 lit. per hour through 2 p.c. sodium hydroxide solution : $2F_2 + 2NaOH = 2NaF + F_2O + H_2O$. The colourless gas is collected over water and liquefied by liquid air, b.p. −146·5°, m.p. −223·8°. It is stable at 125°, has a powerful smell rather like that of fluorine, and is an active oxidising agent, liberating iodine from potassium iodide solution, which absorbs it completely : $F_2O + 4KI + H_2O = 2KF + 2KOH + 2I_2$. Alkalis decompose it with liberation of oxygen without change of volume : $F_2O + 2KOH = 2KF + O_2 + H_2O$, and ammonia evolves nitrogen and forms some nitric acid.

Difluorine dioxide F_2O_2 is an orange-red solid, m.p. −163·5°, formed by the action of an electric discharge on a mixture of fluorine and oxygen at low

temperature and pressure (Ruff, Menzel and Clusius, 1930). Above $-100°$ it decomposes into fluorine and oxygen (Frisch and Schumacher, 1936), not FO as was at first thought.

Chlorine

Glauber (1646) described the preparation of *spirit of salt*, a solution of hydrochloric acid, and sodium sulphate (*Glauber's salt*) from common salt, and in 1658 (*De Natura Salium*) he prepared concentrated hydrochloric acid by distilling salt with sulphuric acid. The solution, which Boerhaave (1732) called *spiritus salis Glauberi*, was afterwards called *marine acid* or *muriatic acid* (Latin *muria*, brine). Priestley in 1772 first collected the gas over mercury.

Scheele (1774) found that manganese dioxide dissolved in cold concentrated marine acid to a brown solution which on warming evolved a greenish-yellow gas with a powerful odour, bleaching action, and strong action on metals. He called it *dephlogisticated marine acid, i.e.* marine acid deprived of hydrogen (which he considered to be phlogiston). Berthollet (1785) supposed that it was *oxygenated muriatic acid* (*oxymuriatic acid*), pointing out that it is formed by the action of oxidising agents on muriatic acid, and that its solution when exposed to sunlight evolves oxygen and leaves muriatic acid. Muriatic acid was regarded by Lavoisier as the oxide of an unknown radical, but in 1789 he said of it: "We have no idea whatever of the nature of its radical and only conclude from analogy with the other acids that it contains oxygen as its acidifying principle."

Gay-Lussac and Thenard in 1809 obtained hydrogen on heating sodium in muriatic acid gas, which they supposed contained water, but they were unable to oxidise strongly heated charcoal by the gas. They rejected an alternative theory that muriatic acid is a compound of hydrogen and oxymuriatic acid (an element) and retained Lavoisier's view.

Davy in 1810 failed to obtain any oxygen compound from oxymuriatic acid and concluded that it is an element, muriatic acid being its compound with hydrogen, and called it *chlorine* (Greek *chloros*, greenish-yellow). He found that phosphorus burns in it to form a liquid (PCl_3) and a solid (PCl_5), that sulphur forms a liquid (S_2Cl_2), but no oxygen compounds are formed. Charcoal heated to whiteness (by the electric arc) in the gas was without action. Dry chlorine does not bleach. All products obtained from oxymuriatic acid weigh more than the gas. (See *Alembic Club Reprints* 9 and 13.)

Preparation of chlorine.—Some metal chlorides on heating evolve chlorine and form the metal or a lower chloride.

Platinic chloride decomposes at 374° into chlorine and platinous chloride, which at 582° gives chlorine and platinum: $PtCl_4 = PtCl_2 + Cl_2$; $PtCl_2 = Pt + Cl_2$. Gold trichloride at 175° forms the monochloride and at 185° this decomposes to the metal: $AuCl_3 = AuCl + Cl_2$; $2AuCl = 2Au + Cl_2$. Dry cupric chloride decomposes slowly at 350° and rapidly at 500° into the stable cuprous chloride and chlorine: $2CuCl_2 = 2CuCl + Cl_2$. Magnesium oxychloride strongly heated in a current of oxygen or air evolves chlorine: $2Mg_2OCl_2 + O_2 = 4MgO + 2Cl_2$.

Many fused metal chlorides are electrolytes and evolve chlorine at the anode, *e.g.* NaCl, AgCl, $ZnCl_2$, $SnCl_2$, $PbCl_2$.

Silver chloride fuses at 460° to a dark yellow liquid and electrolysis with carbon electrodes in a Jena glass U-tube gives pure chlorine (Faraday, 1833; Shenstone, 1897; Dixon and Edgar, *Phil. Trans.*, 1906, **205**, 169). To remove silver crystals bridging the electrodes the current is increased from time to time.

Most chemical preparations of chlorine depend on the *oxidation of hydrochloric acid* by free oxygen or oxidising agents such as manganese dioxide, potassium dichromate, potassium permanganate and bleaching powder: $2HCl + O = H_2O + Cl_2$.

(i) Atmospheric oxygen oxidises gaseous hydrogen chloride on heating in presence of a copper salt as catalyst: $4HCl + O_2 \rightleftharpoons 2H_2O + 2Cl_2$.

EXPT. 1.—A stream of air is passed through concentrated sulphuric acid in a Woulfe's bottle into which concentrated hydrochloric acid drops slowly (Fig. 312).

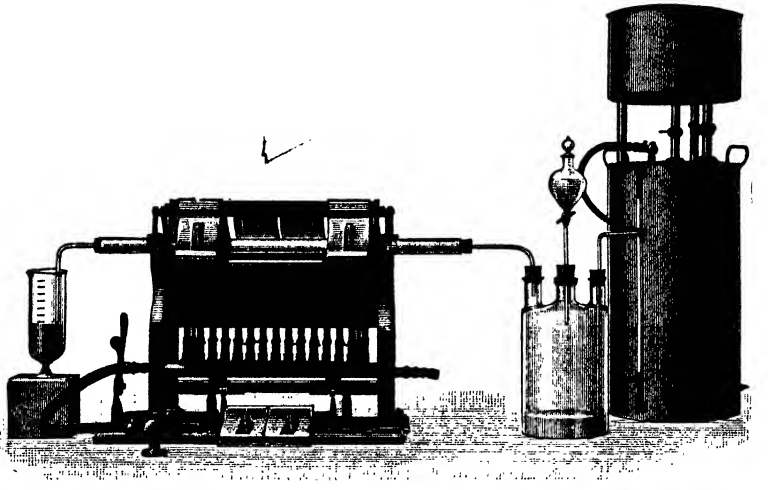


FIG. 312.—Oxidation of hydrochloric acid gas by atmospheric oxygen with formation of chlorine.

The gas is passed through a hard glass tube, packed with pieces of pumice soaked in copper sulphate solution and dried, the tube being heated to dull redness. The gas is passed into litmus solution which is bleached by the chlorine. The copper sulphate is first converted into the chloride: $CuSO_4 + 2HCl = CuCl_2 + H_2O + SO_3$, and this acts as a catalyst, probably by the alternate formation and decomposition of cupric chloride (Hurter, 1877):

$$2CuCl_2 = 2CuCl + Cl_2$$
$$O_2 + 4HCl + 4CuCl = 2H_2O + 4CuCl_2.$$

This is an example of Mercer and Playfair's theory of catalysis (p. 145).

This reaction was formerly used in the industrial *Deacon process* (Deacon and Hurter, 1868); a mixture of air and hydrogen chloride gas was passed over broken bricks previously soaked in copper solution, heated at 450°. The

catalyst slowly became inactive and was renewed. The reaction is reversible and only two-thirds of the hydrogen chloride is decomposed. The rest was washed out with water and the gas (containing only 5 to 10 p.c. of chlorine, diluted with nitrogen) was dried with concentrated sulphuric acid and used to make bleaching powder.

The reaction $4HCl + O_2 \rightleftharpoons 2H_2O + 2Cl_2$ is exothermic and the yield of chlorine decreases with rise of temperature, but the reaction is slow below 425°; the optimum temperature is 470°. The equilibrium constant $K' = p_{Cl_2}^2 p_{H_2O}^2 / p_{HCl}^4 p_{O_2}$ is given by the equation: $\log K' = 6034/T - 6{\cdot}972$ (T = abs. temp.) and has the following values at 1 atm. pressure:

$t°$ C. -	-	352		450	480	650
$\log K'$	-	2·494	1·610	1·454	1·340	−0·380

(ii) The usual laboratory method for the preparation of chlorine is by heating *manganese dioxide* (*pyrolusite*) with concentrated hydrochloric acid: $MnO_2 + 4HCl = MnCl_2 + 2H_2O + Cl_2$.

EXPT. 2.—100 g. of pyrolusite in small pieces in a two-litre flask with a black rubber stopper is covered with 300 c.c. of conc. hydrochloric acid and the flask heated gently. The chlorine is washed with a little water and collected in dry jars by downward displacement (it is 2½ times as heavy as air). It may also be collected over saturated brine, which dissolves 0·36 its volume of chlorine. If required dry, the gas is passed through concentrated sulphuric acid. Chlorine attacks mercury but can be kept over concentrated sulphuric acid. The preparation is carried out in a good draught cupboard, as the gas has a powerful corrosive action on the mucous membranes, which is somewhat relieved by the inhalation of alcohol vapour and dilute ammonia gas. The dark brown solution formed in the cold contains a higher chloride of manganese, probably $MnCl_3$, which decomposes on warming:

$$2MnO_2 + 8HCl = 2MnCl_3 + Cl_2 + 4H_2O$$
$$2MnCl_3 = 2MnCl_2 + Cl_2.$$

A mixture of 5 parts of powdered MnO_2, 11 of common salt and 14 of 50 p.c. H_2SO_4 gives a slow steady stream of chlorine in the cold and a more rapid evolution on heating (Berthollet, 1785; Klason, 1890):

$$4NaCl + MnO_2 + 3H_2SO_4 = Cl_2 + 2NaHSO_4 + Na_2SO_4 + MnCl_2 + 2H_2O.$$

This reaction was formerly used technically, the manganese being recovered from the solution containing $MnCl_2$ by the *Weldon process* (1866), modifying a process of Gossage (1837).

Manganous hydroxide was precipitated by adding a 30–40 p.c. *excess* of milk of lime: $MnCl_2 + Ca(OH)_2 = Mn(OH)_2 + CaCl_2$. Air was blown through the suspension at 60°. The manganous hydroxide oxidised to the weakly acidic manganese dioxide, which combined with the excess of lime, a strong base, to form *calcium permanganite* CaO,MnO_2, or $CaMnO_3$. On adding more manganese liquid and blowing more air, black *calcium dipermanganite* $CaO,2MnO_2$, or $Ca(Mn_2O_5)$, called *Weldon mud*, was formed, which was decomposed by hydrochloric acid to make chlorine. Excess of lime was essential, otherwise the MnO_2 reacted with the basic $Mn(OH)_2$ to form manganous permanganite MnO,MnO_2 or Mn_2O_3.

(iii) *Potassium dichromate* gently heated with concentrated hydrochloric acid evolves nearly pure chlorine :

$$K_2Cr_2O_7 + 14HCl = 2KCl + 2CrCl_3 + 7H_2O + 3Cl_2.$$

(iv) A convenient (but rather expensive) method of preparing pure chlorine is to drop concentrated hydrochloric acid on *potassium permanganate* at room temperature (C. F. Cross and Graebe, 1902) :

$$2KMnO_4 + 16HCl = 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2.$$

EXPT. 3.—Drop concentrated hydrochloric acid slowly on crystals of potassium permanganate in a flask. Chlorine evolved in the cold is washed with water and concentrated sulphuric acid, and a further supply is obtained on warming. By passing this gas into a glass bulb cooled in solid carbon dioxide and ether liquid chlorine is formed, by the evaporation of which very pure chlorine is obtained (Partington, 1914).

(v) A cheap method is to drop a mixture of equal volumes of concentrated hydrochloric acid and water on *bleaching powder* :

$$CaOCl_2 + 2HCl = CaCl_2 + Cl_2 + H_2O.$$

This gas may contain carbon dioxide (from $CaCO_3$ in the bleaching powder).

Electrolytic chlorine and alkali.—Practically all the chlorine made industrially is produced by the electrolysis of salt brine. The Cl′ ions migrate to the anode and are discharged ; the Cl atoms form Cl_2 which escapes as gas. The sodium ions migrate at the cathode and are discharged as atoms, which either react with water to form sodium hydroxide solution and hydrogen : $2Na + 2H_2O = 2NaOH + H_2$, or, if the cathode is mercury, dissolve in it to form sodium amalgam, which can afterwards react with pure water. Of the many types of electrolytic cell (see Partington, *The Alkali Industry*, 1925, Sect. V) two based on these principles will be described.

(i) The *Gibbs cell* (Fig. 313) used by the United Alkali Co. at Widnes has a cylindrical perforated iron cathode separated from the brine by a diaphragm of asbestos paper. The anodes are carbon rods from which chlorine gas is evolved. The sodium hydroxide solution formed on the outside of the cathode flows away, the brine level inside being kept up. The solution contains some sodium chloride which is separated as solid by concentration, the remaining caustic soda solution being evaporated and fused (p. 302).

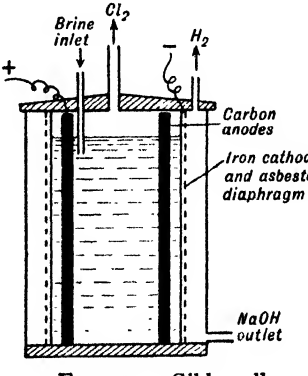


FIG. 313.—Gibbs cell.

(ii) The *Castner-Kellner cell* with a layer of mercury moved by rocking is now replaced by the *Solvay trough cell*. In this, Acheson graphite anodes dip into the brine and the cathode is a layer of mercury on the slate base of the cell (Fig. 314). This mercury flows slowly through the cell and brine flows in the same direction.

Each unit is small and several of them are used. The chlorine is mostly evolved from the anodes as gas which is collected and liquefied, but some remains in solution. The sodium ions discharge on the mercury in preference to hydrogen ions, which have a large overvoltage on mercury (p. 122), and the sodium atoms

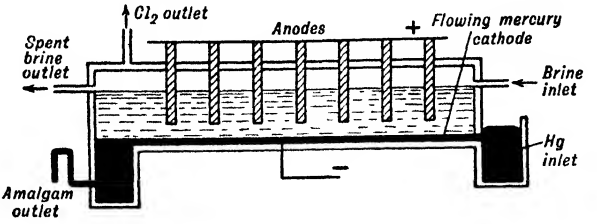


FIG. 314.—Solvay cell.

dissolve to form sodium amalgam. This runs from the cell into a vessel of water in which it comes in contact with metallic iron on which hydrogen has only a very small overvoltage. The arrangement behaves as a short-circuited cell: $^{-}Na,Hg \mid NaOH$ sol. $\mid Fe^{+}$.

Sodium atoms pass into solution as ions: $Na = Na^{\cdot} + e$ and the electrons travel through the mercury to the iron, on the surface of which they discharge hydrogen ions from the water ($H_2O \rightleftharpoons H^{\cdot} + OH'$) to form hydrogen atoms, which combine to form molecular hydrogen which escapes as gas: $H^{\cdot} + e = H$; $2H = H_2$. The hydroxide ions of the water remain with the sodium ions to form a solution of sodium hydroxide. When this reaches 40 p.c. it is evaporated and the caustic soda (which is very pure) is fused in iron pots (p. 302). The mercury freed from sodium re-enters the electrolytic cells, and circulates constantly.

The pure electrolytic chlorine is liquefied by compression or cooling in iron apparatus and is sold in steel cylinders or tanks, which are not attacked by *dry* chlorine. Chlorine gas is used in making stannic chloride, chlorinated acetylenes (p. 455), sulphur chloride, carbonyl chloride, hypochlorite solutions for bleaching and petroleum refining, in sterilising water, in liberating bromine (p. 799), and in making synthetic hydrochloric acid (p. 778).

Properties of chlorine.—Chlorine is a greenish-yellow gas, about $2\frac{1}{2}$ times as heavy as air, with a suffocating and corrosive action on the mucous membranes, and is poisonous. The density is slightly higher than corresponds with Cl_2 (perhaps a little Cl_4 is present), but becomes normal at 240° and remains normal up to 1200° at least. At higher temperatures some dissociation occurs: $Cl_2 \rightleftharpoons 2Cl$.

Reinganum (1905) found that equal volumes of gas were expelled from a small quartz Victor Meyer apparatus at 1150° whether filled with oxygen or chlorine. Crafts (1880) had obtained the same result by displacing oxygen with chlorine or chlorine with oxygen in a porcelain apparatus at 1350°. Victor Meyer and Langer (1885) found a fall in density at 1400° to 29·29 (H = 1), corresponding with 21 p.c. dissociation, but this value is probably too large. Pier (1908) from the change of specific heat with temperature assumed some dissociation above 1450°. At very low pressures the dissociation is appreciable at

700°–900° (Henglein, 1922). Some *calculated* values for the p.c. dissociation of halogens at 1 atm. press. are (Zeise, 1934) :

$T°$ abs.	500	1000	1500	2000	Ht. of dissoc. k. cal./mol.
Cl_2 - -	5×10^{-9}	$2{\cdot}5 \times 10^{-2}$	3·5	35·3	56·9
Br_2 - -	2×10^{-7}	0·30	15·2	53	45·23
I_2 - -	1×10^{-4}	2·88	52	95	35·39

Chlorine is fairly easily liquefied. When cooled in solid carbon dioxide and ether it forms an amber-yellow *liquid*. On cooling in liquid air this forms a pale yellow *solid*. The gas is liquefied at 0° by 3·66 atm. pressure, at −34·5° by 1 atm., and at 20° by 6·57 atm.

Chlorine is very active and combines directly with hydrogen and most metals and non-metallic elements except nitrogen, oxygen (it reacts with ozone, when exposed to light, to form Cl_2O_6), and carbon (except finely divided, at 400°, when CCl_4 is formed). Reaction often occurs with moist chlorine at room temperature with flame and incandescence.

Reaction with metals does not always occur with *dry* chlorine, although pure dry mercury absorbs pure dry chlorine (Shenstone, 1897). Andrews (1842) found that copper and zinc do not react with dry chlorine (see Newth, *Chemical Lecture Experiments*, 1915, 86, for details), but reaction occurs with phosphorus, arsenic and antimony. Bromine behaves similarly. Sodium can be melted without reaction in dry chlorine (Wanklyn, 1869 ; Cooper, 1883 ; Dixon, *J.C.S.*, 1896, **69**, 774). In the following experiments, therefore, undried chlorine should be used.

EXPT. 4.—Sprinkle powdered arsenic and antimony into jars of chlorine ; they burn, producing poisonous fumes of $AsCl_3$ and $SbCl_5$. Leaves of Dutch metal inflame.

A piece of phosphorus in a deflagrating spoon inflames in a jar of chlorine, burning with a pale flame to fumes of PCl_5.

EXPT. 5.—Pass chlorine over a piece of sodium strongly heated in a hard glass bulb tube. The metal burns with a very brilliant yellow flame forming NaCl.

EXPT. 6.—A burning jet of hydrogen burns in a jar of chlorine with an enlarged greenish flame, forming fumes of hydrogen chloride. A jet of chlorine burns with a green needle-shaped flame when passed into an inverted jar of hydrogen burning at the mouth.

Since chlorine has a strong affinity for hydrogen but practically none for carbon, hydrocarbons burn in chlorine with formation of hydrogen chloride and liberation of free carbon.

EXPT. 7.—A burning *taper* continues to burn in chlorine with a small dull red flame, evolving fumes of hydrogen chloride and black clouds of carbon.

A mixture of 2 vols. of chlorine and 1 vol. of *methane*, made by bringing suitable jars of the gases together and sliding out the plates, burns, when kindled, with a dull red flame, fumes of hydrogen chloride and black carbon being formed : $CH_4 + 2Cl_2 = C + 4HCl$.

A mixture of 2 vols. of chlorine and 1 vol. of ethylene burns, when kindled, with a dull red flame, evolving fumes of hydrogen chloride and a very dense black cloud of carbon : $C_2H_4 + 2Cl_2 = 2C + 4HCl$.

A little warm turpentine poured on filter paper and put into a jar of chlorine inflames and burns with a smoky flame, evolving fumes of hydrogen chloride and black carbon : $C_{10}H_{16} + 8Cl_2 = 10C + 16HCl$.

Chlorine combines directly with sulphur dioxide, carbon monoxide and ethylene, forming sulphuryl chloride SO_2Cl_2, carbonyl chloride $COCl_2$, and ethylene dichloride $C_2H_4Cl_2$, respectively. The carbon monoxide and sulphur dioxide react in presence of charcoal, all the gases in presence of sunlight.

Atomic chlorine is formed by an electric discharge in chlorine at low pressure. It reacts rapidly with hydrogen in the dark and slowly with many non-metals and metals (Schwab and Friess, 1933 ; Willey and Foord, 1934).

Chlorine water.—Chlorine is fairly soluble in water, 2·68 vols. in 1 vol. of water at 15°. The vols. reduced to 0° and 760 mm. total pressure (gas + water vapour) dissolved by 1 vol. of water are :

0°	10°	15°	20°	25°	30°	40°	50°	60°
4·61	3·095	2·635	2·260	1·985	1·769	1·41	1·20	1·0

Below 9·6° saturated solutions are metastable and supersaturated with respect to solid chlorine hydrate, in presence of which the solubility is a maximum, 2·98 vols., at 9·6°.

The solution (*chlorine water*) is pale yellow, smells strongly of the gas, and has oxidising and bleaching properties, which have been explained as due to *nascent* oxygen liberated from the water : $H_2O + Cl_2 = 2HCl + O$. *Dry* chlorine does not bleach, as may be shown by suspending some dry red flannel in a jar of chlorine containing some concentrated sulphuric acid. Chlorine water precipitates sulphur from hydrogen sulphide : $H_2S + Cl_2 = S + 2HCl$, and liberates iodine from potassium iodide : $2KI + Cl_2 = 2KCl + I_2$; with excess of chlorine the iodine dissolves to form iodine chloride ICl. Sulphur dioxide is oxidised to sulphuric acid : $SO_2 + Cl_2 + 2H_2O = H_2SO_4 + 2HCl$.

A flask of chlorine water inverted in a dish of the liquid when exposed to bright sunlight decomposes with evolution of oxygen : $2H_2O + 2Cl_2 = 4HCl + O_2$. In less intense light some chloric acid is formed :

$$5Cl_2 + 5H_2O = HClO_3 + 9HCl + O_2.$$

Saturated chlorine water, and solid chlorine hydrate in a sealed tube, are not decomposed by light (Pedler, *J.C.S.*, 1890, **57**, 613 ; Wöhler, *Annalen*, 1853, **85**, 374).

Chlorine is more soluble in concentrated hydrochloric acid than in water, and heat is evolved, hence HCl_3 may be formed. In chloride solutions (*e.g.* NaCl) it is less soluble than in water.

Chlorine hydrate.—When chlorine is passed into water cooled in ice, pale greenish-yellow crystals of *chlorine hydrate* separate (Berthollet, 1785 ; Pelletier, 1785). Its composition has been given as $Cl_2,10H_2O$ (Faraday),

$Cl_2,8H_2O$ (Roozeboom, 1884), $Cl_2,7H_2O$ (de Forcrand, 1902), and $Cl_2,6H_2O$ (Bouzat and Azinières, 1923; Anwar-Ullah, *J.C.S.*, 1932, 1172). When gently warmed the crystals melt and evolve pure chlorine (Harker, 1892). In a sealed tube the crystals are stable below 28·7°, when they melt with formation of liquid chlorine, and chlorine water.

The water-chlorine system (Fig. 315) has been examined by Roozeboom (1884). There are two components and since $P = C + 2 - F$, when $F = 0$ *four* phases form an invariant system at a quadruple point. The possible phases are (i) two *solids*, ice and chlorine hydrate, (ii) two *liquids*, solution I of water in liquid chlorine, and solution II of chlorine in water, and (iii) one *gas* phase (chlorine and water vapour).

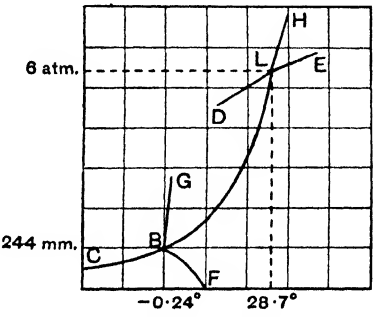


FIG. 315.—The water-chlorine system.

There are two *invariant systems* ($F = 0$) with *four phases*: (i) at the point L (28·7°, 6 atm.), which is a quadruple point where chlorine hydrate decomposes into ice, solution I, solution II, and vapour, and (ii) at the point B (−0·24°, 244 mm.), which is a quadruple eutectic point with the phases ice, chlorine hydrate, solution II, and vapour.

The *univariant systems* ($F = 1$) with *three phases* are represented by seven curves:

BL	chlorine hydrate, solution II, and vapour;
DL	chlorine hydrate, solution I, and vapour;
LE	solution I, solution II, and vapour;
LH	chlorine hydrate, solution I, and solution II;
CB	chlorine hydrate, ice, and vapour;
BF	ice, solution II, and vapour;
BG	ice, chlorine hydrate, and solution II.

The *bivariant systems* ($F = 2$), with *two phases*, are represented by the areas between the curves.

HYDROGEN CHLORIDE

Only one stable compound of hydrogen and chlorine is known, HCl. Hydrogen chloride or hydrochloric acid (the last name is commonly used for the solution) occurs in some volcanic gases and in rivers near volcanoes; 0·2–0·4 p.c. is found in gastric juice and as much as 3 p.c. in the dog's gastric juice.

Hydrogen chloride is made in the laboratory by heating common salt with concentrated sulphuric acid:

$$NaCl + H_2SO_4 = NaHSO_4 + HCl.$$

The reaction $NaCl + NaHSO_4 = Na_2SO_4 + HCl$ occurs at a temperature (over 500°) which cannot be reached in a glass flask without danger of cracking.

With a Kipp's apparatus charged with concentrated sulphuric acid and lumps of sal ammoniac a regular stream of gas is evolved.

EXPT. 8.—Place 25 g. of dry salt in a 500 c.c. flask and pour in through a thistle funnel 25 c.c. of concentrated sulphuric acid. A rapid evolution of gas occurs and when this slackens the flask may be gently heated. The gas is passed through a small wash-bottle containing concentrated sulphuric acid and collected in dry jars by downward displacement (it is 1·27 times as heavy as air and very soluble in water). It may be collected over mercury. When the jar is full dense white fumes with an irritating acid smell issue from the mouth, formed from minute droplets of solution which have a lower vapour pressure than the water vapour in the air. The gas should not be dried by phosphorus pentoxide as this slowly absorbs it, 1 g. of P_2O_5 taking up 227 c.c. of dry gas (Bailey and Fowler, *J.C.S.*, 1888, **53**, 755): $2P_2O_5 + 3HCl = POCl_3 + 3HPO_3$.

Hydrogen chloride is evolved by the action of concentrated sulphuric acid on many metal chlorides, *e.g.* of sodium, potassium, ammonium, magnesium and calcium; lead, silver, cuprous and mercurous chlorides are decomposed only slowly by the hot acid, and mercuric chloride is not decomposed.

Hydrogen chloride is formed by the action of water on chlorides of boron, aluminium (anhydrous), silicon, tin (stannic), titanium, phosphorus, arsenic, antimony (pentachloride), and phosphorus oxychloride ($POCl_3$), thionyl chloride ($SOCl_2$) and sulphuryl chloride (SO_2Cl_2). The pure gas is obtained by the action of water on silicon tetrachloride: $SiCl_4 + 2H_2O = SiO_2 + 4HCl$, and removing any chlorine by passing over dry mercury: the gas from sodium chloride and concentrated sulphuric acid contains traces of hydrogen sulphide (Gray and Burt, *J.C.S.*, 1909, **95**, 1033).

Hydrochloric acid is *manufactured*: (i) synthetically by burning electrolytic chlorine in electrolytic hydrogen in large vertical silica tubes: $H_2 + Cl_2 = 2HCl$, and dissolving the gas in distilled water, or by passing steam and chlorine over active charcoal as a catalyst: $2Cl_2 + 2H_2O = 4HCl + O_2$; (ii) as a by-product in the manufacture of sodium sulphate (*salt-cake*, p. 314).

Hydrogen chloride is a stable gas but is slightly dissociated at high temperatures: $2HCl = H_2 + Cl_2$.

$t°$ C.	427	727	1537	1727
p.c.	$1·1 \times 10^{-5}$	$1·34 \times 10^{-3}$	0·274	0·41

It is decomposed slightly by electric sparks, ultra-violet light, and radium emanation.

Hydrogen chloride extinguishes a burning taper. Burning sodium continues to burn in the gas with a bright yellow flame: $2Na + 2HCl = 2NaCl + H_2$.

The gas when passed through a tube cooled in liquid air condenses to a white crystalline solid (which sometimes shows pink patches). There are two forms of the solid with a transition point at −174·7°. The solid melts at −111·4° to a colourless liquid, which when dry is without action on magnesium, zinc, iron, quicklime, and some carbonates, all of which are dissolved by the aqueous acid, but it readily dissolves aluminium with evolution of hydrogen. It dissolves iodine.

Hydrogen chloride is very soluble in water : 1 vol. of water at 15° dissolves 458 vols. of gas. The great solubility may be shown by the " fountain experiment " (*College Course*, p. 157). 1 kg. of water saturated with hydrogen chloride at 15° forms 1·75 kg. of 43 p.c. solution, density 1·231. The concentrated acid sold contains about 39 p.c. HCl, density 1·20.

If the gas is passed into a flask of distilled water kept cool by running water from a ring of perforated lead pipe (much heat is given out) a solution of the acid —*spirit of salt*—is produced. The concentrated solution fumes strongly in air.

p.c. HCl	Density D_4^{15}	p.c. HCl	Density D_4^{15}
2·14	1·010	24·78	1·125
10·17	1·050	29·57	1·150
15·16	1·075	34·42	1·175
20·01	1·100	39·11	1·200

Hydrogen chloride forms a solution of maximum boiling point (110° at 760 mm.), the composition of which varies with the pressure (p. 60 ; Roscoe and Dittmar, 1859 ; Bonner and Titus, *J.A.C.S.*, 1930, **52**, 633) :

p. mm. Hg. -	50	250	500	700	760	800	1000	1220	1800
p.c. HCl -	23·42	21·88	20·92	20·36	20·222	20·16	19·73	19·36	18·7

By saturating a strongly cooled solution with the gas three *solid hydrates* are formed : HCl,H_2O (m.p. − 15·35°), $HCl,2H_2O$ (m.p. − 17·7°) and $HCl,3H_2O$ (m.p. − 24·4°) (Rupert, *J.A.C.S.*, 1909, **31**, 851). The solid compounds Cl_2,HCl (m.p. − 115°) and $Cl_2,2HCl$ (m.p. − 121°) are known (Wheat and Brown, *J.A.C.S.*, 1940, **62**, 1577).

Composition of hydrogen chloride.—The composition of hydrogen chloride may be demonstrated both by analysis and by synthesis.

EXPT. 9.—By *electrolysis* of hydrochloric acid of s. g. 1·1 with carbon electrodes (chlorine attacks platinum) equal volumes of hydrogen and chlorine are evolved when the liquid is saturated with chlorine (Fig. 316).

According to Faraday (1833) concentrated hydrochloric acid diluted with 9 to 15 vols. of water gives " only a little oxygen with much chlorine at the anode." Bunsen and Roscoe (1858) detected an evolution of some oxygen with 23 p.c. acid ; with stronger acid it is inappreciable. Dixon found the gas from concentrated hydrochloric acid contained 49·7 p.c. of chlorine and 50·3 p.c. of hydrogen by vol., and 0·1 c.c. of O_2 per lit. Haber and Grünberg (1898) found an appreciable oxygen liberation with 0·1 *N* acid, and in dilute acids chloric acid is formed at the anode.

EXPT. 10.—Hydrogen chloride gas is slowly decomposed by liquid sodium amalgam in the closed limb of the apparatus shown in Fig. 317, and half the volume of hydrogen remains after levelling with mercury. (The whole apparatus must be dry, but Gray and Burt

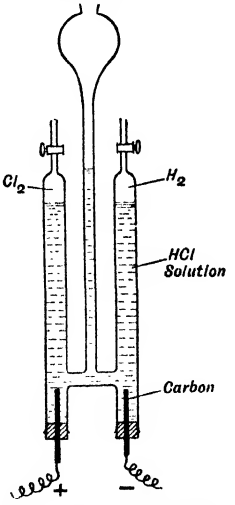


FIG. 316.—Electrolysis of hydrochloric acid.

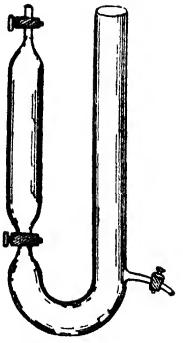


FIG. 317.—Decomposition of hydrogen chloride by sodium amalgam.

say the action of sodium amalgam is inappreciable even at 200° unless the gas is somewhat moist.) Thus, *hydrogen chloride contains half its volume of hydrogen, i.e.* one molecule contains half a molecule or one atom of hydrogen, hence the formula is HCl_x. The density gives the molecular weight 36·5, hence this contains 36·5 − 1 = 35·5 parts, or one atom of chlorine, and the formula is HCl. This agrees with the result of electrolysis.

Gray and Burt (*J.C.S.*, 1909, **95**, 1633) decomposed pure hydrogen chloride with heated aluminium and found that 2 vols. of gas gave 1·0079 vols. of hydrogen, both at S.T.P.

A bulb *M* containing a silica boat which could be heated to dull redness by a platinum-iridium spiral, and containing small pieces of pure aluminium, was connected with the bulb *A* of the apparatus described on p. 671 by a side tube (Fig. 318).

Two vols. of pure hydrogen chloride were passed from *A* (306·849 c.c.) into *M*, and the hydrogen formed in *M* was passed back into *A*, the excess over 1 volume being determined by running mercury from the volume adjuster *J* (p. 672). No correction for hydrogen chloride adsorbed on the walls of *A* was necessary, as the gas was passed from *A* into *M* at atmospheric pressure, and gas adsorbed on the walls of *A* was removed by evacuating before passing in the hydrogen. Since the volume, pressure and temperature of the hydrogen chloride, and the pressure and temperature of the hydrogen were fixed and constant, the mercury run from *J* was a direct measure of the excess x over 1 vol. of hydrogen in 2 vols. of HCl, no corrections being necessary.

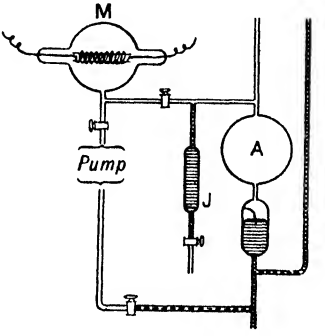


FIG. 318.—Decomposition of hydrogen chloride by heated aluminium.

Volume of HCl = 2 × 306·849 c.c. in all cases; volume of hydrogen = 306·849 + x, where x varied from 2·390 to 2·446, the mean giving 1·00790 vols. of H_2 from 2 vols. of HCl, with a maximum deviation of 1 in 5000.

The normal density of hydrogen chloride was found (p. 10) to be 1·63915, and with Morley's value 0·089873 for the normal density of hydrogen, the molecular weight of hydrogen chloride on the standard H = 1 is

$$(1{\cdot}63915 \times 2)/(0{\cdot}089873 \times 1{\cdot}00790) = 36{\cdot}191,$$

and hence Cl = 35·191, agreeing with the limiting density value (p. 12) to 1 in 7000. With Morley's value for the atomic weight H = 1·00762, the atomic weight of chlorine on the standard O = 16 is 35·191 × 1·00762 = 35·459. Moles (*Z. phys. Chem.*, 1925, **115**, 83) recalculated the physico-chemical values to Cl = 35·458.

The composition of hydrogen chloride may be found by *synthesis* from hydrogen and chlorine. The gas mixture combines slowly in weak light (diffused daylight), and explosively on exposure to bright light or on sparking (even the very dry mixture is exploded by a spark). Hydrogen burns in chlorine, and chlorine in hydrogen (p. 775).

EXPT. 11.—One half of a tube shown in Fig. 319 is filled with hydrogen and the other with chlorine. The gases are allowed to mix by opening the middle stopcock, and the mixture is exposed to *weak* daylight. The greenish colour of the chlorine slowly disappears. The tube is dipped under mercury and a tap opened; it is seen that there has been no change of volume of the gas, but on opening under water this dissolves the hydrogen chloride and fills the tube.

FIG. 319.—Tube for combination of hydrogen and chlorine.

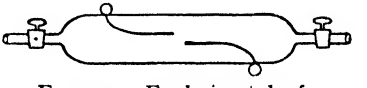


FIG. 320.—Explosion tube for hydrogen and chlorine.

EXPT. 12.—The mixture of hydrogen and chlorine evolved by the electrolysis of hydrochloric acid of s. g. 1·1 (Fig. 322) is passed for half an hour through a strong glass tube fitted with two stopcocks and platinum wires (Fig. 320). The electrolysis should be allowed to go on in a dark room with a photographic lamp. The tube is kept wrapped in black paper until required. Support the tube in a clamp behind a strong glass screen in a dimly-lighted room and fire the gas by a spark from a coil. When the tube is cool open one stopcock under mercury. The volume of gas is unchanged. Open under water; the gas dissolves practically completely.

These experiments prove that 1 *volume of hydrogen combines with* 1 *volume of chlorine to produce* 2 *volumes of hydrogen chloride.* Hence *two* molecules of hydrogen chloride are formed from one molecule of chlorine and one molecule of hydrogen, $H_2 + Cl_2 = 2H_xCl_y$, and the molecular formula of the gas is HCl. This agrees with the density.

The *gravimetric composition* of hydrogen chloride was determined by Dixon and Edgar (*Phil. Trans.*, 1906, **205**, 169) by direct synthesis, in an apparatus constructed on the same principle as Morley's (p. 669), the hydrogen chloride being weighed in solution in water.

Hydrogen absorbed in palladium in a weighed glass bulb was driven out by heating and burnt in a weighed glass bulb containing some water and filled with pure chlorine (prepared by the electrolysis of fused silver chloride) from the liquid in a weighed bulb, the gas being ignited at a jet by a spark. The hydrogen chloride formed dissolved in the water and its weight was thus found. Corrections for residual gas and for some oxygen formed from the water by the action of chlorine were made.

The method was improved by Edgar (*Phil. Trans.*, 1909, **209**, 1) by burning the dry gases in a silica bulb and liquefying and weighing the hydrogen chloride in a separate nickel-plated steel bomb.

The apparatus is shown in Fig. 321. The barrel of the stopcock *e* of the chlorine bulb is inverted so that the pressure maintains it gas-tight. The chlorine was kindled at the silica jet in the atmosphere of hydrogen in the silica bulb by an electric spark, and burned in the hydrogen with a needle-shaped flame. The hydrogen chloride was solidified in the lower extension of the combustion bulb by immersion in liquid air. The residual hydrogen was pumped

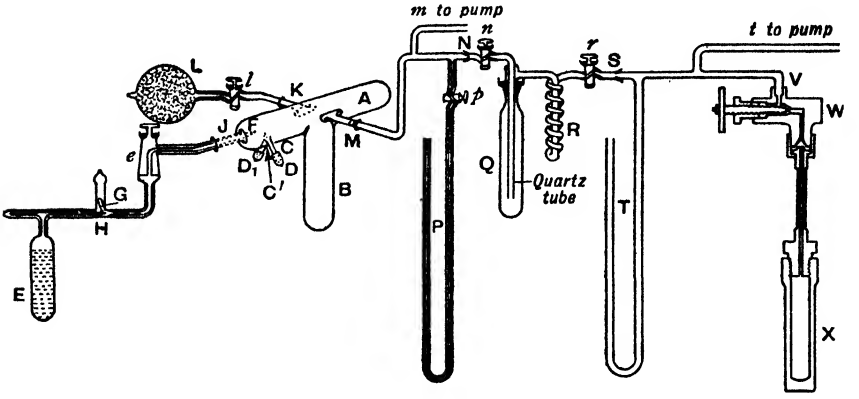


FIG. 321.—Atomic weight of chlorine: Edgar's apparatus.

out and measured. The hydrogen chloride was then evaporated and the gas passed through a silica test-tube containing boiling mercury to free it from chlorine, the mercury vapour being condensed in a cooled glass spiral; the chlorine combined with the mercury was determined by weighing the tube and spiral. The hydrogen chloride gas then passed on to and condensed in a nickel-plated steel bomb cooled in liquid air. The bomb was closed by a needle valve, allowed to warm to room temperature and weighed. (It would have been better to have weighed the hydrogen chloride adsorbed on charcoal, as in Gray and Burt's experiment, p. 10).

The weights of chlorine combining with 1 part of hydrogen were found to be 35·188 to 35·194, the mean being 35·1935. With Morley's value H = 1·00762, this gives Cl = 35·4615 (O = 16).

Photochemical union of hydrogen and chlorine.—A mixture of nearly equal volumes of hydrogen and chlorine, containing a trace of oxygen, is obtained by the electrolysis of hydrochloric acid (s. g. 1·1) with carbon electrodes. The washed gas is passed for at least half an hour through a series of *very thin* glass bulbs (Fig. 322) in a dark room lighted by a ruby lamp. The two ends of the bulbs are closed with soft

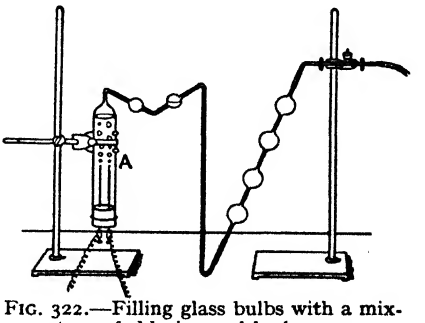


FIG. 322.—Filling glass bulbs with a mixture of chlorine and hydrogen.

wax and the *capillaries* separating them *carefully* sealed off with a small flame. The combustion does not usually spread from the heated part. The bulbs are kept in a dark box.

EXPT. 13.—A bulb containing the mixture of hydrogen and chlorine, protected by a screen of plate glass (Fig. 323), is exposed to the light of burning magnesium flash-powder. A sharp explosion occurs and the glass is shattered. A similar bulb filled with gas dried by passing over P_2O_5 does not usually explode, but the gases combine, as may be shown by opening under litmus solution.

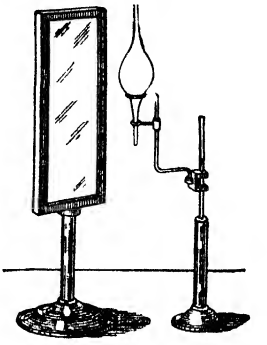


FIG. 323.—Explosion of a mixture of hydrogen and chlorine.

According to Thos. Thomson the explosion of a mixture of hydrogen and chlorine on exposure to sunlight was discovered by Dalton, who communicated it to him by letter in 1809 before the publication of the experiments of Gay-Lussac and Thenard.

Pringsheim (1887) found that the mixed gas after drying with phosphorus pentoxide combined without explosion on exposure to light. Following experiments of H. B. Baker (1894), Coehn and Tramm (1923) found that a pure and carefully dried mixture did not change on exposure to visible light but a partial pressure of 10^{-6} mm. of water vapour was sufficient to initiate the reaction. With ultra-violet light (λ less than 3000 A.) reaction occurred with very dry gases. Other experimenters (Allmand, etc., *J.C.S.*, 1937, 1889) report that dry gas on exposure to light combines as readily as moist, and the difficulty of excluding traces of moisture and inhibitors in this reaction is considerable.

Dixon and Harker (1890) found that the velocity of the detonation wave (p. 472) in carefully dried gas was somewhat greater (1795 m./sec.) than in moist gas (1770 m./sec.), although it is more difficult to start a reaction in dry gas.

J. W Draper (1843), using an apparatus he called a tithonometer (Dixon, *J.S.C.I.*, 1906, **25**, 145) confirmed an effect noticed by Dalton (1809), that a mixture of hydrogen and chlorine did not contract at once when exposed over water to light. There was an initial " hesitation " or period of *photochemical induction*, unless the chlorine was first exposed to light separately. Bunsen and Roscoe, in a classical research (*Phil. Trans.*, 1857–62) used an apparatus called an *actinometer* (Fig. 324). The mixed gas was confined in the half-blackened flat bulb *i* over chlorine water. On exposure to light contraction occurred, the HCl formed dissolving, and the rate of combination was measured by the movement of the thread of liquid in the horizontal tube *k*. They confirmed Draper's result that the rate of combination was proportional to the light intensity, and also noticed the period of induction.

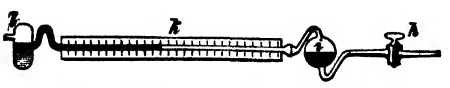


FIG. 324.—Bunsen and Roscoe's actinometer

Burgess and Chapman (1904; *J.C.S.*, 1906, **89**, 1399), however, found that the induction period was (as had been suggested by van't Hoff) due to traces of impurities, particularly ammonia and nitrogen chloride (formed by the action of chlorine on organic nitrogenous matter in the water). By first boiling the water in contact with chlorine these impurities are destroyed, and the mixed gas confined over such purified water at once began to combine on exposure to light. The induction period is not peculiar to the reaction, but is due to impurities. In Draper's apparatus, but not in Bunsen and Roscoe's, these impurities were destroyed when the chlorine was exposed to light before mixing with the hydrogen. Oxygen was found to retard the velocity of combination, but it does not give rise to an induction period.

Einstein in 1912 assumed that the *primary process* in a photochemical reaction is the absorption of one quantum (p. 226), $\epsilon = h\nu$, where ν is the frequency of the radiation, by each reacting molecule. The quantum is larger the smaller the wave-length and light of shorter wave-length (blue, violet, and ultra-violet) has long been known to be, generally, chemically more active than light of longer wave-length (yellow or red). It should be noted, however, that, provided the light will act at all, a given quantity of energy of radiation contains more quanta the smaller the frequency, or the longer the wave-length, and it should therefore, by Einstein's *law of photochemical equivalence*, cause a larger amount of photochemical change than the same quantity of radiant energy of shorter wave-length.

A single quantum of light of wave-length 5400 A., it is believed (Noddack, 1924), can be detected by a normal eye fully adapted in darkness.

Although some reactions agree with the simple form of the law of photochemical equivalence, many show a larger yield. The *primary process* is then followed by *secondary reactions* which occur spontaneously with liberation of energy, *e.g.* in the formation of ozone (p. 658). If the products of the primary reaction are re-formed in a cycle of changes, a **chain reaction** results, in which the quantum efficiency, or number of molecules changed per quantum, would be infinite unless the chain is broken by collision with a foreign molecule (*e.g.* oxygen in the hydrogen-chlorine reaction) or the walls of the vessel. In the hydrogen-chlorine reaction at least a million molecules of hydrogen chloride can be formed by one quantum absorbed. Nernst suggested the following mechanism:

I. Primary (quantum) reaction (absorbs energy): $Cl_2 + h\nu = 2Cl$.

II. Secondary reactions (exothermic):

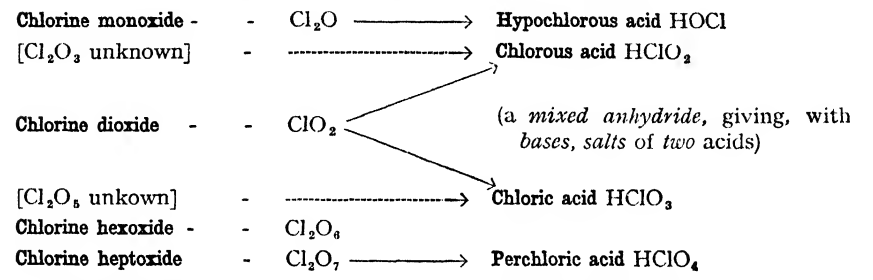
$$\left.\begin{array}{l} Cl + H_2 = HCl + H \\ H + Cl_2 = HCl + Cl. \end{array}\right\} \rightarrow$$

When atomic hydrogen or atomic chlorine is added to the $H_2 + Cl_2$ mixture, more hydrogen chloride than corresponds with its amount is formed, showing that reaction chains are set up in the gas.

If the reaction velocity is due to chlorine *atoms* (as assumed) it should be proportional to the square root of the light intensity, since each quantum forms *two* atoms, and this is found to be the case with very pure gases, free from oxygen (Chapman and Gibbs, 1931; Norrish, *et al.*, *Proc. Roy Soc.*, 1933, **140**, 99, 112, 713).

In some reactions *photosensitisation* occurs. Phosgene $COCl_2$ is a colourless gas absorbing only in the ultra-violet region and therefore, according to the **Grotthuss-Draper law** (1818, 1841) that only rays which are absorbed produce chemical change, is not decomposed by visible light. If chlorine, which absorbs blue light, is mixed with phosgene and the mixture exposed to ordinary light, the phosgene is decomposed by the energy absorbed by the chlorine, which acts as a *photochemical sensitiser*: $COCl_2 = CO + Cl_2$. The combination of hydrogen or sulphur dioxide with oxygen is also sensitised by chlorine.

Oxides and Oxy-acids of Chlorine



Chlorine monoxide Cl_2O, discovered by Balard (1834) by dehydrating hypochlorous acid with calcium nitrate: $2HOCl \rightleftharpoons Cl_2O + H_2O$, is best prepared (Pelouze, 1843) by passing a slow stream of dry chlorine through a cooled tube containing a long layer of precipitated mercuric oxide which has been previously heated to 300°–400° (Fig. 325). (The red oxide reacts too slowly; the precipitated oxide is too active and decomposes the Cl_2O.) Brown mercuric oxychloride and chlorine monoxide are formed:

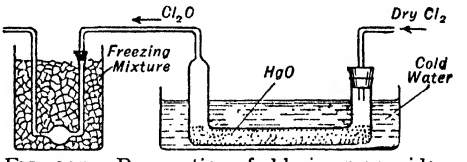


FIG. 325.—Preparation of chlorine monoxide.

$$2Cl_2 + 2HgO = HgCl_2,HgO + Cl_2O.$$

The brownish-yellow gas condenses in a freezing mixture to an orange-coloured liquid, b.p. 2·0°, m.p. −120·6° (Goldschmidt and Schüssler, *Ber.*, 1925, **58**, 569). The gas dissolves in water and attacks mercury, and may be collected by downward displacement.

Cl_2O is said to be formed by the action of a silent discharge on a mixture of chlorine and oxygen (Comanducci, 1910), but this may give Cl_2O_6 (p. 792).

The gas explodes (not very violently) on heating, two vols. giving a mixture of 2 vols. of chlorine (absorbed by alkali) and 1 vol. of oxygen; hence if the formula is Cl_xO_y we have $2Cl_xO_y = 2Cl_2 + O_2$, $\therefore x = 2$ and $y = 1$ and the formula is Cl_2O. The density is slightly higher than corresponds with this.

The liquid may explode on scratching the tube containing it with a file; if free from organic matter it is not decomposed by light and may be distilled without decomposition, but it detonates violently in contact with rubber.

Hydrogen chloride decomposes the gas: $Cl_2O + 2HCl = 2Cl_2 + H_2O$. Chlorine monoxide dissolves in water to a solution containing hypochlorous acid: $Cl_2O + H_2O \rightleftharpoons 2HOCl$, which is golden-yellow when concentrated but colourless when dilute: it evolves Cl_2O on heating.

Hypochlorous acid HOCl (Balard, 1834) is known only as a crystal hydrate $HOCl,2H_2O$, m.p. $-36°$ (Secoy and Cady, *J.A.C.S.*, 1940 **63**, 1036) and in solution.

The solution may be prepared in various ways:

(1) By shaking chlorine water with yellow precipitated mercuric oxide:

$$2Cl_2 + H_2O + 2HgO = HgCl_2,HgO + 2HOCl,$$

distilling, and collecting the hypochlorous acid solution in a cooled receiver. The maximum concentration is about 25 p.c.

(2) By the direct oxidation of hydrochloric acid: $HCl + O = HOCl$. A current of air is passed through concentrated hydrochloric acid and the mixture of air and hydrogen chloride is passed through permanganate solution heated on a water bath, when hypochlorous acid distils (Odling, 1860).

(3) By the hydrolysis of chlorine: $Cl_2 + H_2O \rightleftharpoons HOCl + HCl$. Since the reaction is reversible, the hydrochloric acid formed must be removed, *e.g.* by passing chlorine into a solution of a hypochlorite, sodium sulphate, bicarbonate or phosphate, or a suspension of precipitated calcium carbonate (Williamson, 1845; Richardson, *J.C.S.*, 1908, **93**, 280). The OCl', SO_4'', and HPO_4'' ions form HOCl, HSO_4' and H_2PO_4'; and HCO_3' and CO_3'' form H_2CO_3 and CO_2.

(4) A convenient preparation is to distil bleaching powder solution with the calculated amount of dilute nitric acid:

$$Ca(OCl)_2 + 2HNO_3 = Ca(NO_3)_2 + 2HOCl,$$

or with boric acid (Gay-Lussac, 1842; Taylor and Bostock, *J.C.S.*, 1912, **101**, 444).

A clear solution of bleaching powder is treated with the calculated amount of 5 p.c. nitric acid, added from a burette with constant stirring. The liquid is then distilled.

Since hypochlorous acid is decomposed by hydrochloric acid: $HOCl + HCl \rightleftharpoons Cl_2 + H_2O$, an excess of any acid capable of liberating hydrochloric acid from the calcium chloride in the bleaching powder solution sets free all the chlorine as such:

$$Ca(OCl)_2 + CaCl_2 + 2H_2SO_4 = 2CaSO_4 + 2H_2O + 2Cl_2.$$

Hypochlorous acid solution has a peculiar sweetish smell distinct from that of chlorine. It is a weak acid: $K = [H^{\cdot}]\,[OCl']/[HOCl] = 1 \times 10^{-8}$ at 25° (Soper, *J.C.S.*, 1924, **125**, 2227). Hypochlorites are hydrolysed: $OCl' + H_2O \rightleftharpoons HOCl + OH'$, and $[HOCl]\,[OH']/[ClO'] = 10^{-6}$ at 25°. The dilute solution is fairly stable in the dark but decomposes in sunlight with evolution of oxygen and chlorine and the formation of some chloric acid:

(i) $2HOCl = 2HCl + O_2$; (ii) $HCl + HOCl = Cl_2 + H_2O$; (iii) $HOCl + 2O(\text{nasc.}) = HClO_3$.

The decomposition is accelerated by platinum black, manganese dioxide, or cobalt oxide.

Hypochlorous acid precipitates silver nitrate solution (chloric and perchloric acids do not):

$$3HOCl + 3AgNO_3 = AgClO_3 + 2AgCl + 3HNO_3.$$

Hypochlorous acid and bleaching powder solution dissolve magnesium with evolution of hydrogen; iron and aluminium evolve hydrogen and chlorine; copper, nickel and cobalt evolve chlorine and oxygen (White, *J.S.C.I.*, 1903, **22**, 132).

Hypochlorous acid is an oxidising and bleaching agent, probably owing to the liberation of nascent oxygen. The equations: $Cl_2 + H_2O = 2HCl + O$ and $HOCl = HCl + O$ show that hypochlorous acid, for the same weight of chlorine, has twice the oxidising activity of free chlorine. Hence no loss of activity occurs when chlorine is absorbed by alkali, when a hypochlorite is formed: $Cl_2 + 2OH' = OCl' + Cl' + H_2O$.

Hypochlorous acid and free chlorine are present in equilibrium in chlorine water: (1) $Cl_2 + H_2O \rightleftharpoons HOCl + H' + Cl'$, the hydrolysis constant at 25° being $[HOCl]\,[H']\,[Cl']/[Cl_2] = 4{\cdot}5 \times 10^{-4}$. When chlorine water is boiled under a reflux in a stream of chlorine its composition is unchanged (Richardson, *J.C.S.*, 1903, **83**, 380), but on heating in an open vessel the reaction (1) is reversed and chlorine is evolved.

Jakowkin (*Z. phys. Chem.*, 1899, **29**, 613) determined the hydrolysis constant by the equivalent conductivity: in 0·02308 molar Cl_2 at 0° this was $\lambda = 129{\cdot}5$. As the conductivity is almost entirely due to the hydrochloric acid, for which $\lambda_\infty = 250$ at 0°, the degree of hydrolysis is $129{\cdot}5/250 = 0{\cdot}518$. In 0·05 and 0·01 molar solutions the values were 0·30 and 0·70. The results were confirmed by the distribution coefficient of Cl_2 between CCl_4 and chlorine water: $k = c_1/(1 - x)c_2$, where x = degree of hydrolysis and c_1, c_2 the concentrations in CCl_4 and water.

Hypochlorous acid and free chlorine may be distinguished, and determined quantitatively, by violently shaking the solution with mercury, when chlorine forms white mercurous chloride insoluble in hydrochloric acid, but hypochlorous acid forms brown mercuric oxychloride, soluble in hydrochloric acid (Wolters, 1873):

$$2Hg + Cl_2 = Hg_2Cl_2$$
$$2Hg + 2HOCl = HgCl_2{,}HgO + H_2O.$$

They may also be determined by reaction with acidified potassium iodide:

$$2KI + Cl_2 = 2KCl + I_2$$
$$2KI + HOCl + HCl = 2KCl + I_2 + H_2O.$$

Each molecule of HOCl removes an equivalent of free acid whilst chlorine does not affect the acidity (Bowen, *J.C.S.*, 1923, **123**, 1203; Spinks, *J.A.C.S.*, 1931, **53**, 3015).

To determine free HOCl in presence of hypochlorite, hydrogen peroxide is added and the hydrochloric acid formed is titrated (Sieverts, 1900):

$$HOCl + H_2O_2 = HCl + H_2O + O_2.$$

Hypochlorites.—When chlorine is passed into alkali hydroxide solution *so that the reaction remains alkaline* a hypochlorite and chloride are formed: $Cl_2 + 2OH' = ClO' + Cl' + H_2O$. The solution (*eau de Javelle*; Berthollet, 1785)

has a smell different from that of chlorine and is used for bleaching and as an antiseptic: "Milton" and "Dakin's solution" are of this type. It is usually made from sodium hydroxide solution and electrolytic chlorine.

A solution of sodium hypochlorite and chloride is also formed by precipitating a solution of bleaching powder with sodium carbonate.

$$Ca(OCl)_2 + CaCl_2 + 2Na_2CO_3 = 2NaOCl + 2NaCl + 2CaCO_3,$$

and by electrolysis of sodium chloride solution so that the chlorine and sodium hydroxide set free at the electrodes are allowed to mix and the liquid is kept cool. The yield is improved by adding a little potassium chromate, which prevents reduction by nascent hydrogen.

Acids, even atmospheric carbon dioxide, liberate the very weak hypochlorous acid from hypochlorite solutions:

$$NaOCl + CO_2 + H_2O = NaHCO_3 + HOCl.$$

Hypochlorites evolve oxygen in presence of cobalt oxide (p. 650): $2OCl' = 2Cl' + O_2$, and with hydrogen peroxide (p. 683): $OCl' + H_2O_2 = Cl' + H_2O + O_2$. With hydrochloric acid they evolve chlorine: $OCl' + Cl' + 2H^{\cdot} = Cl_2 + H_2O$. They may act as oxidising agents in alkaline solution: $OCl' = Cl' + O$.

EXPT. 14.—To chrome alum solution add excess of sodium hypochlorite solution: a yellow solution of chromate is formed:

$$2Cr''' + 3OCl' + 10OH' = 2CrO_4'' + 3Cl' + 5H_2O.$$

Add sodium hydroxide solution to manganous sulphate solution: a white precipitate of $Mn(OH)_2$ is formed. Add sodium hypochlorite solution: black MnO_2 is formed: $Mn(OH)_2 + OCl' = MnO_2 + Cl' + H_2O$. On boiling with excess of alkaline hypochlorite a purple solution of permanganate is formed:

$$2MnO_2 + 3OCl' + 2OH' = 2MnO_4' + 3Cl' + H_2O.$$

Very deliquescent crystals of **sodium hypochlorite** NaOCl, 6 or $7H_2O$ are formed by cooling a concentrated solution (from which sodium chloride has deposited) to $-10°$. These melt at 18° and resolidify on cooling to large crystals of $NaOCl,5H_2O$ (Applebey, *J.C.S.*, 1919, **115**, 1106).

Calcium hypochlorite $Ca(OCl)_2$ is prepared in crystals by passing chlorine into milk of lime and evaporating the clear solution in vacuum. The crystalline hydrate $Ca(OCl)_2,4H_2O$ is first deposited. The commercial product (*maxochlor*) is more stable than bleaching powder, is completely soluble in water, and contains about 74 p.c. available chlorine (theoretical for $Ca(OCl)_2 = 99{\cdot}5$ p.c.). Anhydrous $Ca(OCl)_2$ stabilised with a little $Ca(OH)_2$ is called *perchloron*: it is nearly odourless.

Other hypochlorites are obtained in solution by dissolving oxides in hypochlorous acid solution. They are all unstable and tend to form chlorates and chlorides: $3OCl' = ClO_3' + 2Cl'$ (see p. 793).

Bleaching powder.—Chlorine gas does not react with *quicklime* at ordinary temperature but at a red heat oxygen is evolved: $2CaO + 2Cl_2 = 2CaCl_2 + O_2$. Chlorine is rapidly absorbed by *slaked* lime, forming *bleaching powder* or *chloride of lime* (Tennant, 1799; see Mond, *J.S.C.I.*, 1896, **15**, 713). The

reaction is : $Ca(OH)_2 + Cl_2 = CaOCl_2 + H_2O$, most of the water formed remaining in the powder.

In the manufacture of bleaching powder slaked lime is spread over the floors of closed lead chambers and raked into furrows to expose a large surface. Somewhat diluted chlorine gas is passed in. At first this is rapidly absorbed but the reaction afterwards slows down. The powder is turned over with wooden rakes and the action continued until absorption is complete, which takes 12–14 hours. A shower of lime dust is blown in to absorb the excess of gaseous chlorine. The product usually contains 35–37 p.c. of chlorine present as $CaOCl_2$; that calculated for $CaOCl_2 + H_2O$ is 49. Some free lime is also present.

With very dilute chlorine from the Deacon process a very intimate contact is effected in the Hasenclever apparatus by making the gas traverse lead or iron pipes placed horizontally one above the other, through which the lime is pushed in the opposite direction to the gas by means of screws. In the modern apparatus, due to Moore and Rudge, the screw is omitted and a single large rotating iron cylinder used instead of smaller units. Electrolytic chlorine diluted with air is used and, by suitable regulation and control of temperature in particular zones of the cylinder by water cooling, a bleaching powder of high chlorine content and stable in hot climates is obtained (Conroy, *J.S.C.I.*, 1935, **54**, 121).

The **formula of bleaching powder** has been the object of much research. Dalton (1813) suggested that bleaching powder is a compound of lime and chlorine, CaO,Cl_2, "chloride of lime"; Balard (1834) regarded it as a *mixture* of equimolecular amounts of hypochlorite and chloride, $Ca(OCl)_2 + CaCl_2$; Stahlschmidt (1876) assumed that it contained the compound Ca(OH)OCl, but this contains only 33 p.c. of available chlorine.

Balard's formula requires the presence of much free calcium chloride, but bleaching powder is not very deliquescent, gives up only a little calcium chloride to alcohol, and when treated with successive small quantities of water yields much less chloride in the first parts of the extract than would be expected. Moist carbon dioxide at 70° sets free nearly 90 p.c. of the available chlorine of bleaching powder, whilst it has no action on calcium chloride (Lunge and Schäppi, 1880).

The last reaction could be explained (Kraut, 1882) by the action of chlorine monoxide on calcium chloride, so that it is not quite decisive :

$$Ca(OCl)_2 + CO_2 = CaCO_3 + Cl_2O$$
$$CaCl_2 + Cl_2O + CO_2 = CaCO_3 + 2Cl_2.$$

All these results agree with a formula proposed by Odling (1861), in which the active constituent of bleaching powder is assumed to be *calcium chlorohypochlorite* Ca(OCl)Cl, a mixed salt of hypochlorous and hydrochloric acids :

$$Ca\begin{matrix}OH\\OH\end{matrix} \begin{matrix}HOCl\\+\\HCl\end{matrix} = Ca\begin{matrix}OCl\\Cl\end{matrix} \begin{matrix}H_2O\\+\\H_2O\end{matrix}$$

which in solution decomposes into hypochlorite and chloride,

$$2Ca(OCl)Cl = Ca(OCl)_2 + CaCl_2.$$

O'Shea (*J.C.S.*, 1883, **43**, 410) removed any free chloride from bleaching powder by treatment with alcohol and determined in the residue : (i) total lime CaO, (ii) total chlorine after decomposition of hypochlorite by ammonia, and (iii) hypochlorite chlorine, liberating iodine from potassium iodide. The ratios should be as follows :

	Residue	$\frac{CaO}{\text{total Cl}}$	$\frac{CaO}{\text{hypochlorite Cl}}$	$\frac{\text{hypochlorite Cl}}{\text{total Cl}}$
1. Balard - -	$Ca(OCl)_2$	1 : 2	1 : 2	1 : 1
2. Stahlschmidt -	$Ca(OH)OCl$	1 : 1	1 : 1	1 : 1
3. Odling - -	$Ca(OCl)Cl$	1 : 2	1 : 1	1 : 2
4. Found - -		1 : 2	1 : 1	1 : 2

Thus only Odling's formula agrees with the results.

Ditz, and Neumann, regard the free lime or $Ca(OH)_2$ in bleaching powder as an essential constituent, combined water being also present (*Z. Elektrochem.*, 1926, **32**, 18 ; 1929, **35**, 909). Normal bleaching powder is regarded as the compound $3Ca(OCl)Cl,Ca(OH)_2,5H_2O$. In complete absence of moisture a very hygroscopic compound $3Ca(OCl)Cl,Ca(OH)_2,3H_2O$ is formed, whilst at low temperatures $Ca(OCl)Cl,Ca(OH)_2,H_2O$ can be obtained. The active constituent is Odling's compound $Ca(OCl)Cl$.

Quite a different view is taken by Bunn, Clark and Clifford (*Proc. Roy. Soc.*, 1935, **151**, 141), who assume that the first products of the action of chlorine on slaked lime are a *basic hypochlorite* $Ca(OCl)_2,2Ca(OH)_2$ and a non-deliquescent *basic chloride* $CaCl_2,Ca(OH)_2,H_2O$. On further chlorination, the basic hypochlorite is converted into a mixed crystal consisting mainly of *calcium hypochlorite*, which forms crystals of $Ca(OCl)_2,4H_2O$, recognised microscopically, and ordinary bleaching powder is regarded as a mixture of this and the basic chloride.

Bleaching powder is mostly used as an oxidising agent. If it consisted entirely of $Ca(OCl)Cl$ the chlorine equivalent of the *active oxygen* atom of the hypochlorite would be 2Cl (equivalent to O), *i.e.* the *total chlorine*. This is, in fact, liberated by acids : $Ca(OCl)Cl + H_2SO_4 = CaSO_4 + Cl_2 + H_2O$, and thus behaves as *available chlorine*.

The percentage of available chlorine in bleaching powder is determined (i) by titration with sodium arsenite solution : $As_2O_3 + 2CaOCl_2 = As_2O_5 + 2CaCl_2$, using iodide and starch paper as external indicator ; (ii) by liberation of iodine from potassium iodide acidified with acetic acid and titration with thiosulphate : $2KI + HOCl + CH_3{\cdot}COOH = CH_3COOK + KCl + H_2O + I_2$.

Chlorine dioxide.—T. Hoyle in 1797 obtained a yellow explosive gas by the action of concentrated sulphuric acid on potassium chlorate, and Chenevix prepared it again in 1802. Its composition was first found by Davy in 1815. He showed that 2 vols. on explosion gave 1 vol. of chlorine (absorbable by alkali) and 2 vols. of oxygen, and this result leads to the formula ClO_2 :

$$2Cl_xO_y = Cl_2 + 2O_2,$$

$\therefore x = 1$ and $y = 2$, and the formula is ClO_2. The density just above the b.p. was found by Schacherl (1882) to be slightly higher than corresponds with ClO_2.

In the usual method of preparation, powdered previously fused potassium chlorate is added in small quantities at a time to cooled concentrated sulphuric acid in a small retort. The orange-yellow paste is warmed at 35° and the gas,

which is soluble in water and attacks mercury (which absorbs it completely), is collected by downward displacement. *There is considerable danger of violent explosion in the experiment, which should never be attempted in a school laboratory.* The reaction :

$$3KClO_3 + 2H_2SO_4 = KClO_4 + 2KHSO_4 + H_2O + 2ClO_2,$$

probably involves the decomposition of chloric acid :

$$KClO_3 + H_2SO_4 = KHSO_4 + HClO_3$$
$$3HClO_3 = HClO_4 + 2ClO_2 + H_2O ;$$

or : $$3ClO_3' + 2H^{\cdot} = ClO_4' + 2ClO_2 + H_2O.$$

A non-explosive mixture of chlorine dioxide and carbon dioxide is formed by heating at 60° a mixture of 40 g. of $KClO_3$, 150 g. of oxalic acid crystals and 20 c.c. of water (Calvert and Davis, *J.C.S.*, 1859, **11**, 193 ; Bray, 1906) :

$$2HClO_3 + (COOH)_2 = 2H_2O + 2CO_2 + 2ClO_2.$$

The best method of preparation of pure chlorine dioxide is to pass dry clohrine over silver chlorate at 90° and condense the chlorine dioxide as liquid or solid by passing the resulting gas through a tube in a freezing mixture (King and Partington, *J.C.S.*, 1926, 925) :

$$2AgClO_3 + Cl_2 = 2AgCl + 2ClO_2 + O_2.$$

Chlorine dioxide has a disagreeable smell, described as a mixture of the smells of chlorine and burnt sugar. When cooled the gas condenses to a dark red liquid, and this freezes at the temperature of solid carbon dioxide and ether to a bright red crystalline solid, like potassium dichromate in appearance. Both liquid and solid are slowly decomposed by exposure to light. The liquid is very dangerously explosive but may be distilled in the entire absence of organic matter. When made from potassium chlorate and sulphuric acid the chlorine dioxide, which seems to contain some impurity, may detonate quite capriciously ; the pure compound made from silver chlorate is less likely to do this. The gas readily explodes on heating or on contact with hot glass (according to some experimenters at 60°–63°), or when sparked, and it also explodes in contact with alcohol, ether and turpentine. It liberates iodine from acidified potassium iodide solution :

$$2ClO_2 + 10HI = 5I_2 + 2HCl + 4H_2O,$$

and is a powerful oxidising agent. This is shown by the following experiments (Hoyle, 1797 ; Fourcroy and Vauquelin, 1797).

EXPT. 15.—Equal parts of powdered sugar (or starch) and potassium chlorate are mixed with a spatula on a sand bath, and a drop of concentrated sulphuric acid allowed to fall on the mixture. The mass ignites and burns violently.

EXPT. 16.—A little potassium chlorate is placed in a glass of water with a few small fragments of phosphorus. A few c.c. of concentrated sulphuric acid are *carefully* poured down a thistle funnel on the chlorate. ClO_2 is evolved and in contact with the phosphorus gives a series of flashes of light with slight and (usually) harmless explosions.

Chlorous acid.—Chlorine dioxide dissolves almost unchanged in *water* to a bright yellow solution which is stable for several weeks in the dark at 0°. The fresh solution gives no precipitate of silver chlorite with silver nitrate and the slow reaction which occurs is $6ClO_2 + 3H_2O = 5HClO_3 + HCl$. The distribution ratio of ClO_2 between water and CCl_4 is independent of the concentration, hence the hydrolysis is zero (cf. chlorine water, p. 787) (Bray, *J.C.S.*, 1906, **90**, ii, 222). In *alkali* solution, however, ClO_2 is hydrolysed to chlorate and **chlorite**; $2ClO_2 + 2OH' = ClO_3' + ClO_2' + H_2O$ (Millon, 1843). On evaporation in vacuum of the solution obtained with potassium hydroxide, the less soluble $KClO_3$ is first deposited.

A pure chlorite is best prepared by adding alkali and hydrogen peroxide, or sodium peroxide, to concentrated chlorine dioxide solution. The peroxide reduces chlorine dioxide to chlorous acid: $2ClO_2 + H_2O_2 = 2HClO_2 + O_2$. Barium chlorite is formed by suspending barium peroxide in hydrogen peroxide and passing in chlorine dioxide. Free chlorous acid solution is obtained from barium chlorite and dilute sulphuric acid.

The alkali chlorites bleach, but they may be distinguished from hypochlorites by the bleaching action *after* addition of sodium arsenite, as they react only slowly with it. Sodium chlorite $NaClO_2,3H_2O$ is used for bleaching as *textone*. Silver and lead nitrates precipitate yellow crystalline $AgClO_2$ and $Pb(ClO_2)_2$. These explode on heating; lead chlorite mixed with sugar explodes violently on percussion and has been used for detonators.

Chlorites liberate iodine from iodides, the reaction being complete in presence of boric acid to neutralise the alkali formed:

$$ClO_2' + 4I' + 2H_2O = Cl' + 2I_2 + 4OH',$$

and they give a characteristic violet colour with ferrous sulphate (Lenssen, 1862).

Chlorous anhydride Cl_2O_3 is not known. Millon (1843) and others thought it was formed by warming a mixture of potassium chlorate and sugar or arsenious oxide and nitric acid, but Garzarolli Thurnlackh (*Annalen*, 1881, **209**, 184) showed that the gas was a mixture of chlorine dioxide and chlorine. He measured the expansion ΔV after explosion, and the volume of oxygen v remaining after absorption of chlorine by potassium iodide, and showed that $v = 2\Delta V$, as would be the case with chlorine dioxide: $2ClO_2 = Cl_2 + 2O_2$, but not with Cl_2O_3: $2Cl_2O_3 = 2Cl_2 + 3O_2$ ($v = \Delta V$). The same method had been used by Pebal (*Annalen*, 1875, **177**, 1) to show that euchlorine (p. 794), supposed by Davy to be an oxide Cl_2O, is also a mixture of chlorine and ClO_2.

Chlorine hexoxide Cl_2O_6 was first described by Millon (1843) as separating in dark red drops when chlorine dioxide is exposed to light: he gave it the formula Cl_6O_{17} (instead of Cl_6O_{18}). It was again obtained by Bodenstein, etc. (1925), and is best prepared by mixing ClO_2 and ozonised oxygen at 0°. It is a very dark red liquid like bromine, less explosive than ClO_2, dissolving unchanged in water but forming chlorate and perchlorate with alkali:

$$Cl_2O_6 + 2OH' = ClO_3' + ClO_4' + H_2O,$$

so that the structure may be $O_2Cl^{V} \cdot O \cdot Cl^{VII}O_3$. In solution in CCl_4 the formula is Cl_2O_6; the liquid has a low vapour pressure, and the vapour is unstable

but there is some indication that it contains ClO_3 (Goodeve and Richardson *J.C.S.*, 1937, 294).

Chlorates.—When chlorine reacts with alkali solution only hypochlorite and chloride are formed as long as the liquid is alkaline :

$$(1) \quad Cl_2 + 2OH' = OCl' + Cl' + H_2O,$$

and the solution may be boiled without much change (Gay-Lussac, 1842).

When all the alkali is removed free hypochlorous acid is formed :

$$Cl_2 + H_2O \rightleftharpoons HOCl + HCl$$
$$OCl' + HCl = HOCl + Cl'.$$

Hypochlorous acid oxidises the hypochlorite ion to chlorate :

$$(2) \quad OCl' + 2HOCl = ClO_3' + 2Cl' + 2H^{\cdot},$$

and the hydrogen ions form hypochlorous acid :

$$(3) \quad H^{\cdot} + OCl' = HOCl,$$

which reacts according to (2). By multiplying (1) by 3 and (3) by 2 and adding to (2) we find :

$$3Cl_2 + 6OH' = ClO_3' + 5Cl' + 3H_2O,$$

which is the equation for the total reaction (Lunge and Landolt, *J.S.C.I.*, 1885, **4**, 722 ; Foerster and Jorre, *J.C.S.*, 1899, **76**, ii, 278).

The reactions with bromine are similar but with iodine the hypoiodite ion is rapidly converted into iodate in alkaline solution :

$$3OI' = IO_3' + 2I',$$

and a similar reaction occurs *slowly* on boiling alkaline hypochlorite solution, a chlorite being probably formed as an intermediate stage :

$$2OCl' = ClO_2' + Cl'$$
$$OCl' + ClO_2' = ClO_3' + Cl'.$$

EXPT. 17.—Chlorine gas, washed with water, is passed into a solution of 20 g. of KOH in 40 c.c. of water, the gas being delivered through an inverted funnel to prevent choking of the delivery tube by crystals (Fig. 326). When the liquid smells strongly of chlorine the total reaction :

$$3Cl_2 + 6KOH = KClO_3 + 5KCl + 3H_2O$$

has occurred. On cooling $KClO_3$ crystallises. The mother-liquor is poured

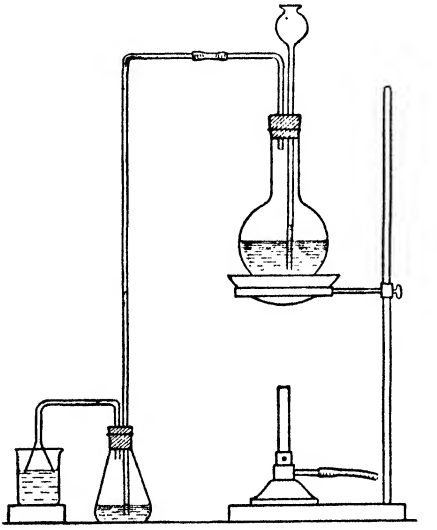


FIG. 326.—The preparation of potassium chlorate.

off and the $KClO_3$ washed with a little cold water and recrystallised from hot water. The chlorate crystals are monoclinic (Fig. 327). On evaporating the mother-liquor cubic crystals of KCl are obtained.

Potassium chlorate is sparingly soluble in cold water but readily in hot; sodium chlorate is very soluble:

	0°	20°	40°	60°	100°
$NaClO_3$ g./100 g H_2O -	81·9	99	123·5	147·1	232·6
$KClO_3$,, ,, -	3·14	7·22	13·31	23·42	55·54

Potassium chlorate (Berthollet, 1787: "oxymuriate of potash") gives certain reactions characteristic of all chlorates.

(1) Solutions give no precipitate with silver nitrate but on heating the dry salt evolves oxygen and the solution of the residue of potassium chloride gives a precipitate of silver chloride: $2KClO_3 = 2KCl + 3O_2$.

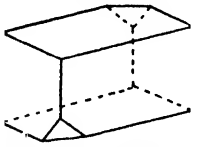


FIG. 327.—Crystal of potassium chlorate.

(2) If a solution of potassium chlorate is mixed with indigo solution and a few drops of sodium sulphite solution, the colour of the indigo is discharged (Frambert, 1857). The chlorate is reduced to a lower oxide of chlorine which has strong bleaching properties.

(3) A *little* potassium chlorate with concentrated sulphuric acid in a test-tube turns orange-yellow and evolves yellow explosive chlorine dioxide, having a peculiar odour: $3KClO_3 + 2H_2SO_4 = KClO_4 + 2KHSO_4 + H_2O + 2ClO_2$. On warming there is a crackling noise, due to explosions of the ClO_2.

(4) Potassium chlorate warmed with concentrated hydrochloric acid evolves yellow *euchlorine* gas, a mixture of Cl_2 and ClO_2:

$$8KClO_3 + 24HCl = 8KCl + 12H_2O + 9Cl_2 + 6ClO_2$$ (see p. 792).

Potassium chlorate detonates violently when triturated with phosphorus or sulphur. (*Dangerous.*) A mixture of chlorate and sulphur detonates on percussion.

Potassium and sodium chlorates are made on the large scale. In one process chlorine in slight excess is passed into hot milk of lime in a cast-iron vat with a stirrer:

$$6Cl_2 + 6Ca(OH)_2 = Ca(ClO_3)_2 + 5CaCl_2 + 6H_2O.$$

The solution is concentrated and cooled, and filtered from the crystals of $CaCl_2,6H_2O$ which separate. Excess of sodium sulphate is added, which precipitates $CaSO_4$. On evaporation of the filtered solution sodium chloride separates and is removed, and on cooling the liquid **sodium chlorate** $NaClO_3$ crystallises. If the solution containing calcium chlorate is warmed with solid potassium chloride, **potassium chlorate** $KClO_3$ crystallises on cooling.

Chlorates are usually made *electrolytically*. The cells are of iron with iron cathodes and graphite anodes. A 25 p.c. KCl solution is electrolysed at 70°–75° till it is nearly saturated with chlorate, when it is cooled and the salt crystallises. Saturated NaCl solution is used at 40° until two-thirds is converted to chlorate, then evaporated, when NaCl first crystallises and then $NaClO_3$. Some alkali

chromate or dichromate is usually added, as it prevents reduction by hydrogen at the cathode. Potassium chlorate is used in making matches and fireworks and sodium chlorate as a weed-killer and in oxidising aniline to aniline black.

Chloric acid $HClO_3$ is known only in solution, but is more stable than hypochlorous acid and is formed when this, or chlorine water, is exposed to light. It was first prepared by Gay-Lussac (1814) by precipitating barium chlorate solution with dilute sulphuric acid :

$$Ba(ClO_3)_2 + H_2SO_4 = BaSO_4 + 2HClO_3.$$

The small excess of sulphuric acid is precipitated with baryta water and the decanted solution evaporated in a vacuum desiccator until it contains 40 p.c. of chloric acid. On further concentration it decomposes :

$$3HClO_3 = HClO_4 + Cl_2 + 2O_2 + H_2O.$$

A solution of potassium chlorate may be precipitated with hydrofluosilicic acid (Serullas, 1830) :

$$2KClO_3 + H_2SiF_6 = K_2SiF_6 + 2HClO_3.$$

Barium chlorate is made by evaporating a solution of sodium chlorate and barium chloride : $2NaClO_3 + BaCl_2 = 2NaCl + Ba(ClO_3)_2$. The sodium chloride is filtered with a hot-water funnel and the filtrate evaporated, when monoclinic crystals of $Ba(ClO_3)_2.H_2O$ separate.

Concentrated chloric acid is a colourless liquid which is fairly stable in the dark. It has a pungent smell, rather like that of nitric acid. When exposed to light it turns yellow and decomposes. It is a powerful oxidising and bleaching agent. Organic substances such as cotton-wool and paper are inflamed by the concentrated acid.

EXPT. 18.—Pour concentrated sodium hydrogen sulphite $NaHSO_3$ solution over potassium chlorate crystals. A trace of free chloric acid is liberated by the weakly acid $NaHSO_3$ and this oxidises the $NaHSO_3$ to the strongly acid $NaHSO_4$. This sets free more chloric acid and the reaction velocity is increased by the action of the products until in a short time the whole mixture foams suddenly.

Chloric acid evolves some hydrogen with zinc, but the acid, and chlorates in acid solution, are easily reduced by iron, aluminium powder, or sulphur dioxide to hydrochloric acid. Perchloric acid is not reduced in dilute solution.

Perchloric acid $HClO_4$ is the most stable oxyacid of chlorine and the only one known in the pure state. It was discovered by Stadion in 1815.

He obtained potassium perchlorate from the residue of the action of sulphuric acid on potassium chlorate (p. 791) and by distilling it with sulphuric acid he prepared 70 p.c. perchloric acid. The formation of perchlorate on heating potassium chlorate was discovered by Serullas in 1831.

Small amounts of sodium perchlorate $NaClO_4$ occur in crude Chile nitre ($NaNO_3$) and cause injury to vegetation when the crude nitrate is used as a fertiliser.

Perchloric acid is formed when chloric acid solution is evaporated or distilled :

$$3HClO_3 = HClO_4 + Cl_2 + 2O_2 + H_2O.$$

It is usually prepared by distilling potassium perchlorate with concentrated sulphuric acid :

$$KClO_4 + H_2SO_4 = KHSO_4 + HClO_4.$$

Potassium perchlorate $KClO_4$ is prepared by heating the *pure* chlorate at 510° in a new porcelain dish, or better at 480° in a silica flask for 8 hours, separating the chloride by cold water, and crystallising the residual perchlorate from hot water (Farmer and Firth, *J.C.S.*, 1924, **125**, 82) : $4KClO_3 = 3KClO_4 + KCl$. Any chlorate remaining may be decomposed by hydrochloric acid, which does not act on the perchlorate, and the latter purified by recrystallising.

Potassium perchlorate forms rhombic crystals (Fig. 328), sparingly soluble in water, whilst sodium perchlorate is deliquescent and very soluble :

	0°	10°	20°	30°	50°
$KClO_4$ g./100 g. H_2O -	0·71	1·08	1·67	2·49	5·34
$NaClO_4$ „ „ -	167·0	—	—	219·6	272·5

Potassium perchlorate decomposes at a higher temperature than the chlorate : $KClO_4 = KCl + 2O_2$, and does not bleach indigo in presence of sulphite ; it gives dense white fumes of perchloric acid when heated with concentrated sulphuric acid, but is not acted upon by hydrochloric acid, and it is not precipitated by silver nitrate.

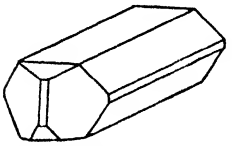


FIG. 328.—Crystal of potassium perchlorate.

Perchlorates, used to make detonators and explosives, are made by electrolytic oxidation of chlorate solutions, oxidation probably occurring with nascent oxygen at the anode : $ClO_3' + O = ClO_4'$.

When potassium perchlorate is distilled with four times its weight of concentrated sulphuric acid in a small retort under atmospheric pressure the perchloric acid collecting in the receiver gradually solidifies to white crystals of the monohydrate $HClO_4,H_2O$, m.p. 50°. *Anhydrous perchloric acid* was first prepared by Roscoe (1861) by distilling the monohydrate at 110°, but it is more directly obtained by distilling potassium perchlorate with 96–97·5 p.c. sulphuric acid at 10–20 mm. pressure at 90°–160°. It is purified by redistilling at 40°–60° under 60 mm. pressure.

Anhydrous perchloric acid is a colourless mobile liquid, s. g. 1·782 at 15°, boiling with some decomposition at 90° under 760 mm. pressure or without decomposition at 19° under 11 mm. pressure. Its m.p. is −112°. It may explode when heated at atm. pressure. On keeping it becomes dark coloured (perhaps from formation of Cl_2O_6) and in a sealed tube it finally explodes. It is an oxidising agent and inflames paper and wood ; when dropped on wood charcoal which has been previously heated and cooled it explodes violently. It fumes strongly in moist air and hisses when dropped into water, owing to the great heat of solution, 20·3 k. cal. per mol. A constant b.p. solution

(72 p.c. $HClO_4$) distils at 203°. The following crystalline hydrates are formed:

$HClO_4,H_2O$ m.p. + 50°. $HClO_4,\frac{5}{2}H_2O$, m.p. − 30°. $HClO_4,3H_2O$, two forms, $HClO_4,2H_2O$, m.p. − 17·8°. $HClO_4,\frac{7}{2}H_2O$, m.p. − 41·4°. m.ps. − 43·2° and − 37°.

The crystalline monohydrate $HClO_4,H_2O$ is apparently *hydroxonium perchlorate* $(H_3O)ClO_4$, as its X-ray spectrum is like that of ammonium perchlorate $(NH_4)ClO_4$ (Volmer, 1924). The Raman spectrum of the anhydrous acid suggests the formula $HO{\cdot}ClO_3$ (Simon, etc., 1938). Perchloric acid forms stable compounds with many organic bases.

The oily aqueous acid is quite stable and is conveniently prepared by adding ammonium perchlorate (a commercial substance) dissolved in concentrated hydrochloric acid to warm concentrated nitric acid in a porcelain dish and evaporating (Willard, *J.A.C.S.*, 1912, **34**, 1480). The reaction is complicated: $34NH_4ClO_4 + 36HNO_3 + 8HCl = 34HClO_4 + 4Cl_2 + 35N_2O + 73H_2O$.

The aqueous acid is used in analysis but some care is necessary; it detonates with great violence when evaporated with alcohol, and is probably not so safe as has been stated.

Perchloric acid is a strong acid, as shown by the electrical conductivity of its solutions. It is not so strong an oxidising agent as chloric acid, and solutions of it dissolve zinc and iron to form perchlorates with evolution of hydrogen: $Zn + 2HClO_4 = Zn(ClO_4)_2 + H_2$, and it is not reduced by nascent hydrogen. It is reduced to chloride by titanium trichloride and in alkaline solution by ferrous hydroxide.

Silver perchlorate is soluble in water and toluene. Magnesium perchlorate $Mg(ClO_4)_2,3H_2O$ is nearly as good a drying agent as phosphorous pentoxide.

Chlorine heptoxide Cl_2O_7, the anhydride of perchloric acid, is obtained by dehydrating anhydrous perchloric acid with phosphorus pentoxide (Michael and Conn, 1900; Goodeve and Powney, *J.C.S.*, 1932, 2078):

$$2HClO_4 + P_2O_5 = Cl_2O_7 + 2HPO_3.$$

Ten g. of P_2O_5 are placed in a small stoppered retort connected with a P_2O_5 drying tube. Pure anhydrous perchloric acid is added ten drops at a time and allowed to trickle down the sides of the retort on the P_2O_5, ten minutes being allowed to elapse between each addition, and the retort kept at − 10° in a freezing mixture. After 24 hours in the freezing mixture the retort is warmed to 85° and chlorine heptoxide distils as a colourless oily liquid into a receiver cooled in ice and salt. Violent explosions may occur in the preparation, but the Cl_2O_7 is not so dangerous as liquid ClO_2.

A safer method of preparation is to heat potassium perchlorate with chlorosulphonic acid under reduced pressure, but the product (98–99 p.c. Cl_2O_7) contains traces of sulphur compounds which cannot be removed (Meyer and Kessler, 1921).

Chlorine heptoxide is more stable than Cl_2O or ClO_2 and may be poured on paper, wood, sulphur or phosphorus without explosion. It explodes when heated or struck and decomposes in a few days. It sinks in water and slowly forms perchloric acid.

CHAPTER XXVIII

BROMINE AND IODINE

Bromine

BROMINE was discovered by A. J. Balard in 1825 (published in 1826) at Montpellier in the residual liquor (*bittern*) after the separation of common salt from sea water by evaporation. It is now made from sea water by the same reaction as served for its discovery, the action of chlorine on the bromides present, the free bromine colouring the liquid orange-yellow: $Cl_2 + 2Br' = Br_2 + 2Cl'$. The element was given its name from the Greek *bromos*, a bad smell; its dark red vapour has a powerful odour somewhat like that of chlorine but more irritating and poisonous.

Silver bromide AgBr occurs in Mexico and Chile; magnesium, calcium and alkali metal bromides in sea water, in some mineral springs in Germany and America, and in the Stassfurt salt deposits. Average sea water contains 0·065 p.c. of bromine, but the Dead Sea (4·8 p.c. of Br_2) and the Utah Salt Lake contain much more, and the Dead Sea is an important source. Traces occur in Northwich brine and rock salt. Organic bromine compounds occur in sea plants and animals; the ancient Tyrian purple (probably first made in Crete), prepared from a shellfish, is a dibromo-indigo.

Bromine is prepared in the laboratory by distilling potassium or sodium bromide with manganese dioxide and dilute sulphuric acid:

$$2KBr + MnO_2 + 3H_2SO_4 = Br_2 + 2KHSO_4 + MnSO_4 + 2H_2O.$$

EXPT. 1.—2·5 g. of powdered KBr and 7 g. of MnO_2 are distilled in a retort with 15 c.c. of H_2SO_4 mixed with 90 c.c. of water. The dark red bromine vapour is condensed in a little water in the receiver to a red solution of bromine and some nearly black liquid bromine settles out.

Bromine vapour acts violently on the mucous membranes and is poisonous. It corrodes cork and rubber. It bleaches moist litmus paper more slowly than chlorine. Liquid bromine should be kept in well-stoppered bottles. It corrodes the skin, which should be well washed with petroleum if it comes in contact with bromine.

Bromine may be purified by distillation over potassium or calcium bromide, which removes chlorine: $2KBr + Cl_2 = 2KCl + Br_2$. Iodine is removed by converting into bromide and precipitating the iodide as cuprous iodide by copper sulphate and sodium sulphite in solution:

$$2Cu^{\cdot\cdot} + SO_3'' + 2I' + H_2O = 2CuI + H_2SO_4.$$

Scott's preparation of pure hydrobromic acid (p. 802) is the simplest way of obtaining a pure bromine compound. Traces of sulphuric and hydrobromic acids in bromine are removed by standing over quicklime and anhydrous calcium bromide and distilling.

Bromine is extracted technically from sea water at Wilmington, North Carolina (Stewart, *Ind. Eng. Chem.*, 1934, **26**, 361). The water is acidified to pH3·5 and chlorinated. The bromine is blown out by a current of air and absorbed in sodium carbonate solution, forming bromide and bromate :

$$3Br_2 + 3Na_2CO_3 = NaBrO_3 + 5NaBr + 3CO_2.$$

On acidifying, the bromine is liberated and is driven out by steam :

$$NaBrO_3 + 5NaBr + 6HCl = 6NaCl + 3Br_2 + 3H_2O.$$

The bromine vapour may also be adsorbed by charcoal. 1800 gallons of the sea water give 1 lb. of bromine.

Bromine is extracted by chlorination from the bromides in the residual liquid (bittern) after crystallisation of potassium and magnesium chlorides from Dead Sea water and Stassfurt salts, and from some American bitterns after crystallisation of common salt. The heated liquor trickles down a packed tower and chlorine and steam are passed in. The bromine vapour escapes at the top and is condensed. The last traces are kept back by moist iron filings, and the bromides of iron formed are precipitated by potassium carbonate to make potassium bromide :

$$FeBr_3 + 2FeBr_3 + 4K_2CO_3 = Fe_3O_4 + 8KBr + 4CO_2.$$

Commercial bromine is purified by careful distillation. Most of it is used to make ethylene dibromide for ethyl petrol containing lead tetraethyl, the lead after combustion forming the volatile lead bromide, which escapes with the exhaust gas. Bromine absorbed in porous sticks of diatomite brick (" solid bromine ") is used as a disinfectant, and bromine compounds are used in medicine, photography, and in the preparation of various organic compounds, *e.g.* methyl bromide for fire extinguishers.

Bromine is a dark red, almost black, heavy liquid (density 3·188 at 0°, 3·119 at 20°) giving a dark red vapour (vapour pressure 150 mm. at 18° ; b.p. 58·7°). The solid (m.p. −7·2°) is dark red and crystalline (rhombic) ; at −252° it is colourless. The vapour density at 228° corresponds with Br_2, at 1050° 6·3 p.c. is dissociated (p. 775) : $Br_2 \rightleftharpoons 2Br$.

Liquid bromine combines vigorously, sometimes explosively, with phosphorus and many metals : the action is more violent than with chlorine *gas*, but liquid chlorine acts very vigorously and chlorine displaces bromine from compounds.

EXPT. 2.—Five c.c. of bromine are poured into a test-glass standing inside a bell-jar over a draught-hole. The top of the jar is closed by a plate with a central hole. A *small* piece of white phosphorus thrown into the liquid causes an *explosion* and is projected from the liquid. Red phosphorus burns quietly with a dull red flame to yellow fumes of PBr_5. Powdered arsenic burns with a reddish-white flame to fumes of $AsBr_3$. A *small* piece of potassium combines *explosively* forming KBr. Sodium does not combine with bromine unless heated to 200° in the vapour, or water is added.

Bromine is less soluble than chlorine in water, 3·6 g. in 100 g. H_2O at 20°, and the solubility decreases with rise of temperature. The freezing point

shows that the molecule in solution is Br_2. Bromine water is stable in the dark, but *slowly* decomposes in bright sunlight: $2Br_2 + 2H_2O = 4HBr + O_2$. Saturated bromine water in a freezing mixture deposits red crystals of **bromine hydrate** $Br_2,10H_2O$ (Harris, *J.C.S.*, 1932, 582). This decomposes at 6·2° into bromine water and bromine.

The hydrolysis of bromine is smaller than that of chlorine (p. 762); at 25° $K = [H^+]\,[Br^-]\,[HOBr]/[Br_2] = 5{\cdot}2 \times 10^{-9}$. Bromine is more soluble in hydrobromic acid and bromide solutions than in water, forming the Br_3^- ion (Worley, *J.C.S.*, 1905, **87**, 1107).

Chloroform, benzene, and carbon disulphide extract bromine from aqueous solution, forming orange-red liquids. The distribution coefficient (p. 58) for CS_2 is about 80 and for CCl_4 about 30, but it increases with the bromine concentration.

Bromine is an oxidising agent, converting sulphurous and arsenious acids to sulphuric and arsenic acids, liberating iodine from potassium iodide, sulphur from hydrogen sulphide, and nitrogen from ammonia. It oxidises formic acid: $H{\cdot}COOH + Br_2 = CO_2 + 2HBr$, the velocity being retarded by the HBr formed (Hammick, etc., *J.C.S.*, 1925, **127**, 2715).

Hydrogen Bromide

Hydrogen bromide or *hydrobromic acid* occurs in volcanic gases. A mixture of hydrogen and bromine vapour does not react, even in bright sunlight, below 300° and is not explosive, but in presence of platinum as a catalyst combination begins at 200°: $H_2 + Br_2 \rightleftharpoons 2HBr$ (Corenwinder, 1852). Heated charcoal also acts as a catalyst. The heat of formation of HBr from gaseous bromine is 11 k. cal. as compared with 22 k. cal. for HCl. The reaction is reversible and a state of equilibrium is reached, but with excess of hydrogen the combination is practically complete.

Expt. 3.—Pure hydrogen is passed slowly through dry bromine in a bubbler at 35°–40°. The mixture of hydrogen and bromine vapour formed is passed through a hard glass tube containing platinised asbestos packed between plugs of glass wool. When the air is expelled the tube is heated to 200°, when reaction usually proceeds without further heating. To remove unconverted bromine vapour (present only when a rapid stream of gas is used) the gas is passed through a tube packed with solid ferrous bromide. It is dried by passing through tubes containing fused calcium bromide. If pure hydrogen bromide is required the gas is cooled by liquid air, when excess of hydrogen passes on and solid hydrogen bromide is obtained. This process, which is a modification of that of Baxter (*J.A.C.S.*, 1931, **53**, 604), is much superior to the use of an electrically heated platinum spiral.

The *thermal dissociation* of hydrogen bromide is greater than that of hydrogen chloride (p. 778) but much less than that of hydrogen iodide (p. 870):

$t°$ C. - -	727	1024	1108	1220
p.c. dissoc. -	0·18	0·50	0·73	1·08

Hydrogen bromide gas is usually prepared by dropping bromine on a paste of red phosphorus and water (Topsöe, 1870). Since the bromine reacts fairly slowly on the phosphorus particles, phosphorus bromide is probably first formed and then hydrolysed : $PBr_5 + 4H_2O = H_3PO_4 + 5HBr$.

EXPT. 4.—Twenty g. of red phosphorus and 40 c.c. of water are put in a flask and 40 c.c. of bromine are added *drop by drop* from a tap funnel (Fig. 329). The gas passes through a U-tube *loosely* filled with broken glass smeared with moist red phosphorus to remove bromine vapour. On adding the first few drops of bromine lambent green flames appear, but not when the air is displaced. At the end of the reaction the flask is gently heated. The gas is collected by downward displacement in a dry jar. It fumes strongly in moist air and (like HCl and HI) has an irritating acid smell. It may be dried over calcium chloride or bromide and collected over mercury. P_2O_5 reacts only very slowly, some $POBr_3$ being formed (Bailey and Fowler, *J.C.S.*, 1888, **53**, 755).

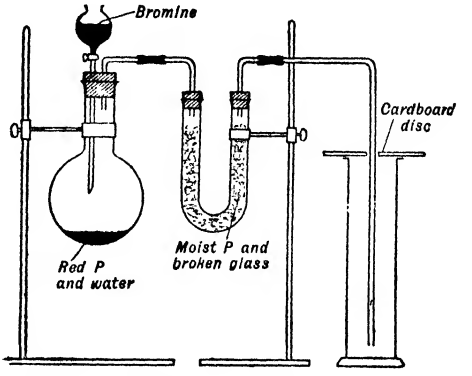


FIG. 329.—Preparation of hydrogen bromide.

Although concentrated sulphuric acid and a bromide evolve hydrogen bromide, *e.g.* $KBr + H_2SO_4 = KHSO_4 + HBr$, the gas is soon contaminated with bromine formed by oxidation of the hydrogen bromide by concentrated sulphuric acid (which cannot be used to dry it), especially on heating : $2HBr + H_2SO_4 = Br_2 + SO_2 + 2H_2O$.

A mixture of 75 g. of powdered KBr with 45 c.c. of concentrated sulphuric acid and 15 c.c. of water gives fairly pure HBr gas on heating, and a solution is formed by distilling KBr with syrupy phosphoric acid, or a mixture of 25 c.c. of a solution of 15 g. of KBr, 3·4 c.c. of sulphuric acid and 0·2 g. of stannous chloride. Hydrogen bromide gas is evolved on dropping bromine into benzene mixed with some iron or aluminium powder, the benzene vapour being removed by passing over anthracene : $C_6H_6 + 2Br_2 = C_6H_4Br_2 + 2HBr$.

Hydrogen bromide is a colourless, strongly fuming gas with a sharp acid smell. The liquid and solid are colourless ; there are two forms of the solid with a transition point at $-183°$. The liquid does not dissolve bromine or iodine. The formula of the gas may be found by the action of sodium amalgam and the density, as in the case of HCl (p. 779).

Hydrogen bromide is very soluble ; 1 vol. of water dissolves 600 vols. of HBr at 0°. The solution is a strong acid : $HBr \rightleftharpoons H' + Br'$. Concentrated hydrobromic acid fumes in moist air. On distillation the solution forms an acid of maximum boiling point 126° at 760 mm., containing 47·5 p.c. HBr.

The composition varies from 47·38 to 47·86 p.c. HBr as the pressure on distil-

lation varies from 752 to 762 mm., and it is not a definite hydrate. The solution saturated at 0° contains 69, that at 25° 66 p.c. of HBr. The solid hydrates $HBr,2H_2O$ (m.p. −11·2°), $HBr,3H_2O$ (m.p. −47·5°) and $HBr,4H_2O$ (m.p. −55·8°) are formed on strong cooling.

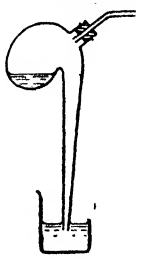


FIG. 330.—Preparation of aqueous hydrobromic acid.

Aqueous hydrobromic acid may be prepared by passing the gas into water through an inverted retort (Fig. 330). If liquid is driven back, it merely collects in the bulb of the retort.

A solution of hydrobromic acid is obtained by passing hydrogen sulphide or sulphur dioxide into bromine covered with a layer of water :

$$Br_2 + H_2S = 2HBr + S$$

$$SO_2 + Br_2 + 2H_2O \rightleftharpoons H_2SO_4 + 2HBr.$$

87·5 c.c. of bromine are covered with 500 c.c. of water in a flask. A current of SO_2 is passed in through a tube just above the bromine until this dissolves to a pale yellow liquid, which is distilled. The liquid is redistilled over $BaBr_2$ to remove any sulphuric acid carried over. This gives pure hydrobromic acid Scott, (*J.C.S.*, 1900, **77**, 648).

Aqueous hydrobromic acid is decomposed by oxygen in sunlight : $4HBr + O_2 = 2H_2O + 2Br_2$, but a dry mixture of hydrogen bromide gas and oxygen is not decomposed by light. The gas or solution is decomposed by chlorine : $2HBr + Cl_2 = 2HCl + Br_2$.

Bromides.—Hydrobromic acid dissolves zinc, iron, and many other metals (including copper when the acid is hot and concentrated) with evolution of hydrogen, forming bromides, which are also obtained by neutralising with oxides, hydroxides, or carbonates, and by the direct combination of metals with bromine.

The alkali bromides are obtained from bromide of iron (p. 799) or by dissolving bromine in alkali solution, evaporating, and heating strongly to decompose the bromate :

$$3Br_2 + 6KOH = 5KBr + KBrO_3 + 3H_2O$$

$$2KBrO_3 = 2KBr + 3O_2.$$

The residue on evaporation may be mixed with powdered charcoal and heated, when the bromate is reduced at a lower temperature :

$$KBrO_3 + 3C = KBr + 3CO.$$

The mass is warmed with water, filtered from excess of charcoal, and crystallised by evaporation.

Ammonium bromide free from bromate is obtained by the action of bromine on cooled ammonia solution : $3Br_2 + 8NH_3 = 6NH_4Br + N_2$.

Nearly all bromides are soluble in water, but cuprous, silver, mercurous, lead and palladous bromides are only very sparingly soluble. Silver nitrate gives a yellowish-white precipitate of AgBr insoluble in dilute nitric acid and

sparingly soluble in *dilute* ammonia but soluble in concentrated ammonia (cf. AgCl and AgI). Palladium nitrate gives a reddish-brown precipitate of palladous bromide $PdBr_2$. The formation of free bromine, soluble in chloroform with a red colour, by the action of chlorine water, and the formation of red bromine vapour when the substance is heated with MnO_2 and H_2SO_4, are also tests for bromides.

Oxides of Bromine

Three unstable oxides of bromine have been described: Br_2O (gas), BrO_2 (solid) and Br_3O_8 (solid), the last being most definite.

Bromine monoxide Br_2O has often been said to be formed in small amount by passing bromine vapour over mercuric oxide (*e.g.* by Zintl and Reinäcker, 1930), and in solution by shaking mercuric oxide with a solution of bromine in carbon tetrachloride (Brenschede and Schumacher, 1935–6).

Bromine dioxide BrO_2 is a yellow solid, stable below 0°, formed by the action of an electric discharge on a mixture of bromine vapour and oxygen in a ratio below 1 : 5 pumped continuously at low pressure through a U-tube with a prolong at the bend cooled in liquid air (Schwarz and Schumacher, 1937).

Bromine peroxide Br_3O_8 is a white crystalline solid (apparently existing in two forms with a transition point at −35°) formed by the action of pure ozone on pure bromine vapour at −5° to +10° under low pressure (Schumacher and Lewis, 1928–9). It is stable at −80°, but unless pure materials and very clean apparatus are used in its preparation it explodes.

Oxyacids of Bromine

Three oxyacids of bromine are known, **hypobromous acid** HOBr and **bromic acid** $HBrO_3$ in solution, and **bromous acid** $HBrO_2$ as salts. Perbromic acid and perbromates are not known.

Hypobromous acid HOBr is formed in solution by shaking bromine water with precipitated mercuric oxide (cf. HOCl):

$$2Br_2 + 2HgO + H_2O = HgBr_2,HgO + 2HOBr.$$

By adding more bromine and mercuric oxide a 6 p.c. solution may be obtained, which may be distilled in vacuum at 40° to give a straw-yellow liquid, always containing some bromine and bromic acid. This decomposes on heating into bromine and bromic acid and is a strong oxidising and bleaching agent.

Hypobromous acid is formed by the action of bromine on concentrated silver nitrate solution and distillation (Pollak and Doktor, 1931):

$$Br_2 + AgNO_3 + H_2O = HOBr + AgBr + HNO_3.$$

An unstable **hypobromite** is formed by dissolving bromine in cold alkali hydroxide solution: $Br_2 + 2OH' = OBr' + Br' + H_2O$. The solution is an oxidising agent, used in the determination of hydrogen peroxide (p. 683) and urea (p. 542). The hypobromite soon forms bromide and bromate: $3OBr' = BrO_3' + 2Br'$. Dry slaked lime absorbs bromine vapour to form red "bromine bleaching powder," and when distilled with dilute nitric acid this gives hypobromous acid.

Bromous acid $HBrO_2$ is unknown but **bromites** are formed in solution by the spontaneous decomposition of hypobromites (Clarens, 1913; Chapin, *J.A.C.S.*, 1934, **56**, 2211): $2BrO' = BrO_2' + Br'$. They rapidly decompose: $3BrO_2' = 2BrO_3' + Br'$. They decompose ammonia, urea and phenol only slowly (distinction from hypobromites) and oxidise arsenites to arsenates (distinction from bromates).

Bromic acid.—When bromine is dissolved in hot concentrated alkali hydroxide solution a bromate and bromide are formed:

$$3Br_2 + 6OH' = BrO_3' + 5Br' + 3H_2O.$$

Potassium bromate is much less soluble than the bromide and separates in hexagonal crystals on cooling. It is also formed by passing bromine vapour into potassium carbonate solution which has been saturated with chlorine:

$$Br_2 + 6OCl' = 2BrO_3' + 4Cl' + Cl_2,$$

and by passing chlorine into alkaline bromide solution:

$$Br' + 6OH' + 3Cl_2 = BrO_3' + 6Cl' + 3H_2O.$$

Silver bromate is formed as a white precipitate on adding alkali bromate to silver nitrate solution, and reacts with bromine water to form bromic acid:

$$5AgBrO_3 + 3Br_2 + 3H_2O = 5AgBr + 6HBrO_3.$$

The filtered solution is concentrated to 5 p.c. of $HBrO_3$ on a water bath and by concentration in a vacuum desiccator a 50 p.c. solution is obtained. More concentrated solutions decompose into bromine and oxygen:

$$4HBrO_3 = 2Br_2 + 2H_2O + 5O_2.$$

Bromic acid is colourless and has a smell of ozone. It is a strong oxidising agent:

$$2HBrO_3 + 5SO_2 + 4H_2O = Br_2 + 5H_2SO_4$$
$$8HBrO_3 + 5H_2S = 4Br_2 + 5H_2SO_4 + 4H_2O$$
$$HBrO_3 + 5HBr = 3Br_2 + 3H_2O.$$

The **bromates** are usually sparingly soluble. On heating they decompose in one of three ways, but perbromates are not formed:

1. $KBrO_3$, $HgBrO_3$, and $AgBrO_3$ give bromide + oxygen;
2. $Mg(BrO_3)_2$, $Zn(BrO_3)_2$, $Al(BrO_3)_3$ give oxide + bromine + oxygen;
3. $Pb(BrO_3)_2$ and $Cu(BrO_3)_2$ give oxide and bromide.

Bromates evolve bromine when heated with concentrated hydrochloric or sulphuric acid:

$$2KBrO_3 + 12HCl = 2KCl + Br_2 + 5Cl_2 + 6H_2O$$
$$4KBrO_3 + 4H_2SO_4 = 4KHSO_4 + 2Br_2 + 5O_2 + 2H_2O.$$

A mixture of $NaBrO_3 + 5NaBr$ is prepared by saturating concentrated caustic soda with bromine and draining the separated crystals. To these sufficient $NaBrO_3$, prepared by electrolytic oxidation of NaBr, is added to form $NaBrO_3 + 2NaBr$, and the mixture (*bromine salt*) is used in the extraction of gold (p. 353).

Barium bromate $Ba(BrO_3)_2,H_2O$ is precipitated on cooling when a slight excess of bromine is added to hot concentrated baryta water :

$$6Ba(OH)_2 + 6Br_2 = Ba(BrO_3)_2 + 5BaBr_2 + 6H_2O.$$

The bromide remains in solution. If barium bromate is digested with dilute sulphuric acid and the excess of the latter removed by baryta water, the filtered solution contains bromic acid.

Iodine

In 1811 Courtois found that the mother-liquors from which sodium carbonate had crystallised in the manufacture from *varec* or seaweed-ashes, when heated with sulphuric acid gave a violet vapour which condensed to a black metallic-looking crystalline substance. This was investigated by Clement and Desormes, and in 1813-14 by Gay-Lussac and simultaneously by Davy (who, by permission of Napoleon, was passing through Paris to Italy at the time). It was recognised as an element analogous to chlorine, and given the name iodine (from the Greek *ioïdes*, violet-coloured) on account of the beautiful violet colour of its vapour.

Although free iodine was detected in the water of Woodhall Spa, near Lincoln, by Wanklyn (1886) iodine otherwise occurs only in compounds. Silver, lead and mercuric iodides occur in Mexico, and iodine is found in some magnesian limestones and dolomites, calcium phosphates and rock salt, in coal, tobacco and other plants, and in some form in the atmosphere (Chatin, 1851 ; Gautier, 1899). Alpine air and glacier waters are poor in iodine.

The iodine content of sea water, partly organic and partly iodide or iodate, never exceeds 0·001 p.c. and in the Atlantic is only 1 part in 280 millions. Seaweeds and sponges absorb it partly as organic compounds : tropical sponges may contain 10 p.c. of iodine and Turkey sponges about 0·2 p.c. The amount of iodine is greater in deep-sea weeds (0·4–0·5 p.c. in the dry weed) than in those growing near the shore (0·1 p.c. or less in the dry weed). During storms these weeds are torn up and cast ashore. They are known in Scotland as *drift-weeds* or *red wracks* ; only *Laminaria digitata* and *L. stenophylla* are used in the preparation of iodine.

Organic iodine occurs in oysters, in cod-liver oil, and as *thyroxin* $C_{15}H_{11}O_4NI_4$ in the thyroid gland (especially of the ray and dogfish, containing 1 p.c. of I). The disease of goitre is caused by deficiency of iodine or inability to assimilate it, and (as shown by Dumas and Coindet in 1818) is prevented and corrected by small amounts of combined iodine, normally present in foods.

Iodides occur in many mineral waters (Leamington, Cheltenham, Woodhall Spa, Montpellier, Heilbrunn, etc.). The salt brine from petroleum wells in Java contains 1·35 g. per lit. of I as iodide, which is precipitated as cuprous iodide (p. 339) and recovered technically. South California petroleum brine (30–70 parts per million of I) is worked for iodine.

Crude Chile saltpetre (*caliche*) contains 0·15–0·2 p.c. of I as sodium iodate $NaIO_3$ (and perhaps periodate $NaIO_4$) and the mother-liquor (*aqua vieja*) from the crystallisation of the sodium nitrate is a source of commercial iodine.

Iodine is prepared in the laboratory by distilling potassium or sodium iodide with dilute sulphuric acid and manganese dioxide :

$$2KI + MnO_2 + 3H_2SO_4 = I_2 + 2KHSO_4 + MnSO_4 + 2H_2O.$$

EXPT. 5.—Heat 3·5 g. of KI with 7 g. of MnO_2 and 100 c.c. of dilute H_2SO_4 (1 : 6) in a retort. The violet vapour condenses in the neck of the retort and in the receiver as glittering black scales of solid iodine.

On the large scale iodine is made from seaweed, brines containing iodides, and from the iodate in the mother-liquor of Chile saltpetre.

Seaweed is burnt in shallow pits and the ash, called *kelp* (*varec* in Normandy), contains potassium salts and from 0·4 to 1·3 p.c. of I as iodide. The preparation of iodine from it was begun by Dr. Ure in Glasgow and is also carried out in Norway and Japan.

The kelp is extracted with hot water and the solution concentrated. The alkali carbonates, chlorides and sulphates crystallise and the mother-liquor contains the very soluble iodides, with some bromides. It is mixed with sulphuric acid and run into iron pots with dome-shaped lead covers communicating with trains of cylindrical earthenware receivers called *udells* (or *aludels*). Manganese dioxide is added, and iodine distils on heating, collecting in the udells. It is purified by sublimation in porcelain pans. About 12 lb. of iodine are obtained per ton of kelp, representing about half that contained in the original weed. In Norway the seaweed is extracted with sodium carbonate solution and on acidification an organic adhesive is precipitated.

The California brine is made faintly acid and sodium nitrite added, which liberates the iodine :

$$2I' + 2NO_2' + 4H^{\cdot} = I_2 + 2NO + 2H_2O.$$

This is adsorbed on active charcoal filters, is extracted from the filters by sodium hydroxide solution, which forms iodide and iodate, and the iodine is set free by acidification (Robertson, *Ind. Eng. Chem.*, 1934, **26**, 376) :

$$3I_2 + 6OH' = IO_3' + 5I' + 3H_2O$$
$$IO_3' + 5I' + 6H^{\cdot} = 3I_2 + 3H_2O.$$

The iodide in the clarified brine may also be precipitated as silver iodide, which precipitates before bromide and chloride, as it is less soluble. The silver iodide is decomposed by iron and water into silver and ferrous iodide.

The mother-liquor of *caliche*, containing iodate, is treated with sodium hydrogen sulphite solution, and the iodine precipitated is pressed and sublimed (Newton, *J.S.C.I.*, 1903, **22**, 469). The reaction has been variously represented but involves reduction of iodate to iodine and oxidation of sulphite to sulphate :

$$2NaIO_3 + 5NaHSO_3 = 3NaHSO_4 + 2Na_2SO_4 + I_2 + H_2O.$$

The reaction occurs in three stages. The iodate is reduced to iodide by a rather slow reaction :

$$(1) \qquad IO_3' + 3HSO_3' = I' + 3HSO_4'.$$

The iodide reacts rapidly with iodate to form iodine :

$$(2) \qquad IO_3' + 5I' + 6H^{\cdot} = 3I_2 + 3H_2O.$$

As long as any sulphite remains, the iodine is reduced to iodide by a very rapid reaction :

$$(3) \qquad I_2 + HSO_3' + H_2O = 2I' + HSO_4' + 2H^{\cdot}.$$

Iodine appears only when the sulphite is used up, and the reaction shows a **period of induction.** This is shown in the following experiment (Landolt, *Ber.*, 1886, **19**, 1317 ; Dushman, *J. Phys. Chem.*, 1904, **8**, 453).

EXPT. 6.—Dissolve 10 g. of crystallised iodic acid in 1 lit. of water. Saturate 5 c.c. of water with sulphur dioxide and add to 1 lit. of water. 50 c.c. of the iodic acid solution are added to 250 c.c. of water in a cylinder with a little starch solution. 50 c.c. of the sulphurous acid are diluted with 250 c.c. of water and poured quickly into the iodic acid. The liquid remains colourless for a certain interval and then at once becomes blue. By varying the dilution the time interval may be altered. According to Landolt the colour appears after $524 \cdot 35/x$ sec. at 20°, where $x = c_{SO_2}^{0 \cdot 904} \cdot c_{HIO_3}^{1 \cdot 642}$ and c = conc. in mols per *cu. metre*. This is an example of *successive reactions* ; the speed of the whole reaction is that of the slowest stage.

Commercial iodine may contain iodine chloride ICl, iodine bromide IBr, and sometimes cyanogen iodide ICN, all of which are volatile and cannot be separated by sublimation. Resublimation over potassium iodide removes most of the impurity : $ICl + KI = KCl + I_2$.

EXPT. 7.—The iodine is ground with half its weight of KI and the mixture gently heated in a porcelain dish on a sand bath with a bolt-head flask filled with water standing on the dish. Glittering crystals form on the flask.

Pure iodine was prepared by Baxter (*J.A.C.S.*, 1922, **44**, 577 ; 1940, **62**, 1829) by decomposing iodine pentoxide (from recrystallised iodic acid) at 300° in a platinum boat in a quartz tube : $2I_2O_5 = 2I_2 + 5O_2$; or by steam-distilling a solution of iodine in potassium iodide.

Properties of iodine.—Iodine crystallises in blackish-grey opaque scales, with an almost metallic lustre, density 4·94 at 18°. When deposited in thin films on glass at −180° it is transparent. Large rhombic crystals (Fig. 331) are formed by spontaneous evaporation of an ether solution, or by allowing concentrated hydriodic acid to oxidise in air.

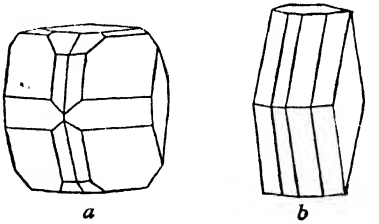


FIG. 331.—Iodine crystals.

Although the vapour pressure at room temperature is small (0·13 mm. at 15°, 0·47 mm. at 20°), iodine has a characteristic smell and in a closed flask the vapour shows a faint colour.

Iodine vapour when pure is deep blue ; when mixed with air it is reddish-violet (Stas). The vapour density at the boiling point 184·4° corresponds with I_2 and remains practically constant to 700°, but then diminishes to 1700°, when according to Victor Meyer it corresponds with complete dissociation : $I_2 \rightleftharpoons 2I$.

Stark and Bodenstein (1910; cf. Perlman and Rollefson, *J. Chem. Phys.*, 1941, **9**, 362) give 45 p.c. dissociation at 1200° and extrapolation indicates complete dissociation only at about 3000°: de Vries and Rodebush (*J.A.C.S.*, 1927, **49**, 656) give, at 1 atm.:

$T°$ abs.	- -	732	823	873	898
p.c. dissociation	-	17·8	50·4	72·1	80·0

Iodine vapour shows an orange-yellow fluorescence, especially when exposed to green light. When exposed to light from a mercury lamp it emits a spectrum of a large number of equally-spaced lines.

Iodine is much less soluble in water than either chlorine or bromine: 0·2765 g./lit. at 18°, 0·4662 at 35° and 0·9226 at 55°. The solution is brownish-yellow. The hydrolysis: $I_2 + H_2O \rightleftharpoons H^{\cdot} + I' + HOI$ is very small; at 25° $[H^{\cdot}]\,[I']\,[HOI]/[I_2] = 3 \times 10^{-13}$. A violet-red crystal hydrate (?) is formed at high pressure only in presence of oxygen or nitrogen (Villard, 1923). Iodine is readily soluble in solutions of hydriodic acid and iodides, forming dark brown solutions containing *tri-iodide ion* I_3'. At 25° $[I']\,[I_2]/[I_3'] = 1{\cdot}36 \times 10^{-3}$ (Jones and Kaplan, *J.A.C.S.*, 1928, **50**, 1845). From potassium iodide solution black crystals of KI_3,H_2O separate, and many other polyiodides are known (p. 305). Chloroform and carbon disulphide do not extract iodine appreciably from such solutions.

Iodine dissolves in many organic liquids. The solution in alcohol is brown: *tincture of iodine* contains ½ oz. each of iodine, potassium iodide and water in rectified spirit to 1 pint.

In methylene iodide the mol. wt. from the freezing point is I_2. Solutions of iodine in carbon disulphide are pure violet, the same colour as the vapour, those in benzene and chloroform are reddish-purple. In these solutions mainly I_2 molecules are present. The purple solution in petrol ether shows colloidal particles in a beam of light, and these are formed in toluene solution on exposure to light.

In water, alcohol, and ether, iodine forms brown solutions, which contain associations of iodine with solvent molecules. A purple solution in chloroform becomes brown on addition of alcohol, but the original colour is restored on dissolving out the alcohol by shaking with water. The purple solution in petrol ether becomes brown when cooled in solid carbon dioxide and ether, but the carbon disulphide solution is unchanged. The brown solution in alcohol shows colloidal particles in a beam of light. Getman (*J.A.C.S.*, 1928, **50**, 2883) states that with *pure* solvents only two colours (violet and brown) are formed.

Iodine combines directly with many elements, forming **iodides**. It explodes with potassium but can be fused with sodium without reaction (cf. Br_2, p. 799). Powdered antimony inflames in the vapour, solid iodine inflames white phosphorus, and when solid iodine is ground in a mortar with the calculated amount of mercury, green mercurous iodide or yellow mercuric iodide is formed according to the proportions used.

Test for iodine.—Solutions of iodine give a beautiful blue colour with starch paste, prepared by warming "soluble starch" with water, or adding boiling water to potato starch made into a paste with cold water. 1 part of iodine in

5,000,000 of water may be detected. The blue colour, described by Colin and Gaultier de Claubry in 1814, disappears on heating, but reappears on cooling.

EXPT. 8.—Add a drop of iodine solution to some dilute starch solution in a test-tube. Heat the tube in a beaker of boiling water : the blue liquid becomes colourless. Cool the lower part of the tube in a beaker of cold water : this part of the liquid again becomes blue.

The blue substance, which is fully developed only in presence of electrolytes, has been variously described as a chemical compound (" iodide of starch "), a solid solution, or an adsorption complex of starch and iodine. A blue colour is produced by the action of iodine on a few other substances, *e.g.* saponarin, cholic acid, euxanthic acid, narceine, basic lanthanum and prascodymium acetates, and moist solid potassium acetate. The reaction is highly specific and is not likely to be due to adsorption or solid solution. Some blue-forming substances are crystalline (Barger, etc., 1912–15 ; Kutzelnigg and Wagner, 1937).

HYDROGEN IODIDE

Hydrogen iodide (hydriodic acid) occurs in some volcanic gases. It is formed when a mixture of hydrogen and iodine vapour is passed over heated spongy platinum or platinised asbestos (Corenwinder, 1852), but the reaction is reversible and incomplete : $H_2 + I_2 \rightleftharpoons 2HI$.

It is formed on heating an alkali iodide with phosphoric acid ; with sulphuric acid oxidation occurs, iodine being set free and some sulphuric acid reduced. Since hydrogen iodide is a more powerful reducing agent than hydrogen bromide the sulphuric acid is reduced not only to sulphur dioxide but also to sulphur and even hydrogen sulphide (Jackson, *J.C.S.*, 1883, **43**, 339 ; Bush, *J. Phys. Chem.*, 1929, **33**, 613) :

$$H_2SO_4 + 2HI = SO_2 + I_2 + 2H_2O$$
$$H_2SO_4 + 6HI = S + 3I_2 + 4H_2O$$
$$H_2SO_4 + 8HI = H_2S + 4I_2 + 4H_2O.$$

Hydrogen iodide is usually prepared by the action of water on a mixture of iodine and red phosphorus (Personne, 1861) :

$$2P + 5I_2 + 8H_2O = 10HI + 2H_3PO_4.$$

EXPT. 9.—Four g. of red phosphorus and 20 g. of iodine are shaken together in a flask and about 15 c.c. of water slowly dropped on from a tap-funnel (Fig. 332). With incorrect proportions of materials phosphine (exploding with air) may be formed.

A more convenient process is to mix 6·5 g. of potassium iodide and

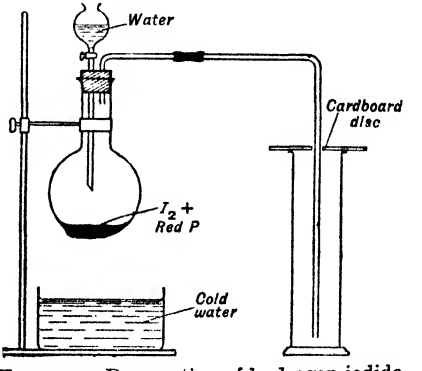


FIG. 332.—Preparation of hydrogen iodide.

13 g. of iodine in 3·3 c.c. of water in a small stoppered retort and add small portions of red phosphorus from time to time, warming if necessary.

The gas may be passed through a U-tube containing broken glass and slightly moist red phosphorus and collected by downward displacement. It is very soluble in water and attacks mercury. (It also attacks heated glass.) It may be dried with calcium chloride or purified phosphorus pentoxide (on which it has no action).

Another method of preparing the gas is to heat a mixture of iodine and colophonium resin.

Hydrogen iodide is a colourless gas fuming strongly in moist air and very soluble in water (425 vols. HI in 1 vol. water at 10°). It liquefies at 4 atm. at 0°, and hence much more easily than hydrogen chloride or bromide. The solid exists in at least two forms with transition points at low temperatures.

The formula is found by the action of sodium amalgam, giving half the volume of hydrogen, and the density, as in the case of hydrogen chloride.

Hydrogen iodide is easily oxidised. A dry mixture with oxygen is decomposed when exposed to light, iodine being set free: $4HI + O_2 = 2I_2 + 2H_2O$. A mixture of 4 vols. of hydrogen iodide and 1 vol. of oxygen burns with a red flame when kindled (Berthelot), and a jet of the gas may be burnt in oxygen in the apparatus used with ammonia (p. 547). A red flame and fumes of iodine are produced when warm fuming nitric acid is poured into a jar of the gas (Hofmann, 1870).

Hydrogen iodide is decomposed on exposure to sunlight: after 10 days 60 p.c. is decomposed and after a year 99 p.c. (Victor Meyer). This photochemical decomposition occurs with the primary reaction: $HI = H + I$ (Bodenstein, 1897, 1908). The thermal decomposition: $2HI \rightleftharpoons H_2 + I_2$ begins very slowly at 180° and becomes faster at higher temperatures. At each temperature a state of equilibrium is reached (Lemoine, 1872; Bodenstein, 1894–9):

$t°$ C. - - -	283	356	444	527	1022
p.c. dissociation -	17·9	19·5	22·0	24·7	32·9

The heat of formation from *solid* iodine is endothermic: $H_2 + I_2(s) = 2HI - 12$ k. cal., but from *gaseous* iodine is exothermic: $H_2 + I_2(g) = 2HI + 9$ k. cal. The heat change in the reaction is small, so that the heat absorbed in the sublimation of solid iodine changes an exothermic into an endothermic reaction. Since heat is absorbed when iodine vapour is formed, the dissociation increases with rise of temperature, in agreement with Le Chatelier's principle (p. 134).

Hydriodic acid solution is prepared by dissolving the gas in water, with the apparatus shown in Fig. 330. The solution saturated at 0°, s. g. 1·99, contains 90 p.c. of HI. The solid hydrates $HI,2H_2O$ (m.p. −43°), $HI,3H_2O$ (m.p. −48°) and $HI,4H_2O$ (m.p. −36·5°) separate on strong cooling.

The solution used as a reducing agent has a s. g. of 1·5. The constant boiling solution (126° at 760 mm.) contains 57 p.c. of HI, hence more concentrated solutions can only be made by dissolving the gas. The fresh solution is colourless but soon becomes brown from oxidation: $4HI + O_2 = 2I_2 + 2H_2O$. This does

not occur on exposure to light in absence of oxygen (Berthelot). The solution may be freed from iodine by distillation over a little red phosphorus.

A less concentrated solution is made by passing hydrogen sulphide into a saturated solution of iodine and adding more iodine as the reaction proceeds :

$$H_2S + I_2 + Aq. = S + 2HI,Aq.$$

Reaction stops when the s. g. of the solution reaches 1·56. The solution is filtered from the sulphur and distilled. Very weak acid (with a little hydrogen sulphide) first distils, then the temperature rises sharply to 126° and the 57 p.c. acid is collected.

The reaction with dry iodine and hydrogen sulphide gas is endothermic and incomplete :

$$H_2S + I_2 \rightleftharpoons S + 2HI - 16{\cdot}8 \text{ k. cal.}$$

The heat of solution of hydrogen iodide gas in a large quantity of water is 19·2 k. cal. per mol, hence the reaction is exothermic in presence of water.

The s. g. of hydriodic acid at about 13° is :

s. g. -	1·077	1·126	1·191	1·254	1·309	1·413	1·528	1·603	1·696	1·708
p.c. HI	10·1	15·7	22·6	28·4	33·1	40·4	48·2	52·4	57·3	57·7

Iodides may be prepared by the same general methods as chlorides and bromides, *e.g.* by the action of iodine or hydriodic acid on metals (hot concentrated hydriodic acid dissolves copper and silver with evolution of hydrogen), by dissolving oxides, hydroxides or carbonates in hydriodic acid, etc. Nearly all iodides are soluble in water, cuprous, silver, mercurous, mercuric, and lead iodides being important exceptions. Silver iodide is formed as a light yellow precipitate insoluble in dilute nitric acid and in *concentrated* ammonia (which dissolves silver chloride and bromide). Other tests for iodides are the formation of violet iodine vapour on heating with manganese dioxide and concentrated sulphuric acid, and of a brown solution after addition of chlorine water, the iodine being extracted as a violet solution on shaking with carbon disulphide or chloroform.

Oxides of Iodine

Iodine forms the solid *oxides* IO_2 (or I_2O_4), I_4O_9 and I_2O_5 ; and the *acids* hypo-iodous acid HOI (known only in solution), iodic acid HIO_3 and three periodic acids HIO_4, $H_4I_2O_9$ and H_5IO_6.

Iodine dioxide I_2O_4 (Millon, 1844 ; Bahl and Partington, *J.C.S.*, 1935, 1258) is formed by heating iodic acid with concentrated sulphuric acid till fumes of iodine appear and decomposing the resulting basic sulphate of iodine with water, in which the dioxide is insoluble. It is a yellow powder, decomposing on heating, rapidly at 130° : $5I_2O_4 = 4I_2O_5 + I_2$. It may be regarded as basic iodine iodate $I^{III}O(I^VO_3)$.

The **oxide** I_4O_9 is formed as a pale yellow deliquescent powder by the action of ozonised oxygen on iodine, when it sublimes (Andrews and Tait, 1859 ; Ogier, 1878 ; Bahl and Partington, 1935). It is decomposed on heating :

$4I_4O_9 = 6I_2O_5 + 2I_2 + 3O_2$, and by water: $5I_4O_9 + 9H_2O = 18HIO_3 + I_2$, which, if I_4O_9 is formulated as iodine iodate $I^{III}(I^VO_3)_3$, may take place in three stages:

(i) $I(IO_3)_3 + 3H_2O = I(OH)_3 + 3HIO_3$,

(ii) $3I(OH)_3 = 2HIO_3 + HI + 3H_2O$,

(iii) $HIO_3 + 5HI = 3I_2 + 3H_2O$.

Iodine pentoxide I_2O_5 (Davy, 1815) is prepared by dehydrating iodic acid: $2HIO_3 = I_2O_5 + H_2O$. The acid is heated at 200°, or at 150° and then in a stream of dry air at 240° (Lamb, Bray and Geldard, *J.A.C.S.*, 1920, **42**, 1636). When pure it is a white powder, s. g. 4·98, decomposed at 300° after fusion: $2I_2O_5 = 2I_2 + 5O_2$, and slowly by light. It is not reduced by hydrogen but readily at 70° by carbon monoxide (Ditte, 1870): $I_2O_5 + 5CO = I_2 + 5CO_2$; this reaction is used to determine traces of CO in air, the CO_2 being absorbed in titrated baryta water; 1 vol. in 30,000 may be determined: a mixture of iodic acid and fuming sulphuric acid reacts similarly. Iodine pentoxide is an oxidising agent and decomposes hydrogen sulphide: $I_2O_5 + 5H_2S = I_2 + 5S + 5H_2O$, and hydrogen chloride: $I_2O_5 + 10HCl = 2ICl_3 + 2Cl_2 + 5H_2O$. It dissolves in water to form iodic acid HIO_3, of which it is the anhydride: $I_2O_5 + 2H_2O = 2HIO_3$.

Oxyacids of Iodine

Hypo-iodous acid HOI is known only in a pale greenish-yellow solution formed by shaking a fine suspension of iodine with precipitated mercuric oxide (Koene, 1845):

$$2I_2 + H_2O + 2HgO = HgI_2,HgO + 2HOI.$$

The solution is decanted or filtered through asbestos from the HgI_2,HgO; it cannot be distilled and rapidly decomposes:

$$5HOI = 2I_2 + HIO_3 + 2H_2O.$$

A brown solution formed by oxidising an iodide with permanganate is supposed to contain I_2,HOI or I_3OH; it does not colour starch blue and iodides precipitate iodine from it: $I_3OH + I' = 2I_2 + OH'$.

A solution of **hypo-iodite** and iodide is formed by dissolving iodine in cold dilute alkali:

$$I_2 + 2OH' = OI' + I' + H_2O.$$

The fresh solution smells of saffron, bleaches indigo, precipitates brown manganic hydroxide from manganous sulphate, oxidises arsenites to arsenates, and gives iodoform with alcohol. The hypo-iodite rapidly decomposes into iodate and iodide: $3OI' = IO_3' + 2I'$, but on acidifying the fresh solution with carbonic acid ("soda-water") up to 97 p.c. of the iodine used is set free (Taylor, *J.C.S.*, 1900, **77**, 725): $OI' + I' + 2H^{\cdot} = I_2 + H_2O$. Hypo-iodous acid is very weak and may be amphoteric:

$$OH' + I^{\cdot} \rightleftharpoons HOI \rightleftharpoons H^{\cdot} + OI'.$$

Iodous acid HIO_2 is not known but may be present in a solution of hypo-iodite: $HOI + OI' = I' + HIO_2$, and as an intermediate stage in the reduction of iodic

acid by hydrogen peroxide : $IO_3' + H_2O_2 = IO_2' + O_2 + H_2O$ (Liebhafsky, *J.A.C.S.*, 1931, **53**, 896).

Iodic acid HIO_3 (Gay-Lussac, 1813), the best known and most stable oxyacid of iodine, is formed by oxidising iodine with ozone in presence of water, but is best prepared by boiling iodine with ten times its weight of very concentrated nitric acid (s. g. 1·5) in a flask, preferably in a current of oxygen (Scott, *J.C.S.*, 1901, **79**, 302) : $3I_2 + 10HNO_3 = 6HIO_3 + 10NO + 2H_2O$.

Nitric acid is eliminated by evaporating to dryness, heating to 200°, and dissolving the iodine pentoxide so formed in the smallest amount of warm water. On cooling the syrupy liquid, crystals of iodic acid separate.

Iodic acid can be prepared by evaporating iodine with 25 p.c. chloric acid (Lamb, etc., *J.A.C.S.*, 1920, **42**, 1636) : $2HClO_3 + I_2 = 2HIO_3 + Cl_2$. It is formed by passing chlorine into a suspension of iodine in water and removing the hydrochloric acid by silver oxide : $I_2 + 5Cl_2 + 6H_2O = 2HIO_3 + 10HCl$, and by precipitating barium iodate with dilute sulphuric acid, or potassium iodate with hydrofluosilic acid. It crystallises more easily from solutions containing a little sulphuric or nitric acid.

Iodic acid forms colourless rhombic crystals, very soluble but not deliquescent. It melts at 110° to form a solution and a solid $3I_2O_5,H_2O$ which is stable to 196°, but then fuses again and forms I_2O_5.

Iodic acid solution first reddens and then bleaches litmus paper. It dissolves zinc, aluminium and iron on warming with evolution of hydrogen : $Zn + 2HIO_3 = Zn(IO_3)_2 + H_2$, ; the nascent hydrogen reduces some iodic acid to iodide. It dissolves copper and silver but not lead, tin, gold and platinum. Iodic acid is an oxidising agent. The solid deflagrates when heated with powdered charcoal, sulphur, phosphorus, or organic matter, and the solution oxidises sulphur dioxide, hydrogen sulphide and hydriodic acid :

$$2HIO_3 + 5SO_2 + 4H_2O = I_2 + 5H_2SO_4$$
$$2HIO_3 + 5H_2S = I_2 + 6H_2O + 5S$$
$$HIO_3 + 5HI = 3I_2 + 3H_2O.$$

Iodates.—Iodine dissolves in hot alkali solution forming an iodate and iodide (Davy, 1813) : $3I_2 + 6OH' = IO_3' + 5I' + 3H_2O$. From potassium hydroxide solution monoclinic (or cubic) crystals of sparingly soluble **potassium iodate** KIO_3 separate on cooling. **Barium iodate** $Ba(IO_3)_2$ (monoclinic) is precipitated from potassium iodate solution by barium chloride ; dilute sulphuric acid decomposes it forming a solution of iodic acid, but this dissolves some barium sulphate : $Ba(IO_3)_2 + H_2SO_4 = BaSO_4 + 2HIO_3$.

Potassium iodate is best made by heating iodine with concentrated potassium chlorate solution and a little nitric acid (Thorpe and Perry, *J.C.S.*, 1892, **61**, 925) : $2KClO_3 + I_2 = 2KIO_3 + Cl_2$.

EXPT. 10.—30 g. of $KClO_3$ dissolved in 60 c.c. of warm water, 35 g. of iodine, and 2 c.c. of concentrated nitric acid are heated gently in a 200 c.c. flask till vigorous reaction begins. When no more chlorine is evolved the liquid is boiled

with 1 g. of iodine, evaporated and cooled. The KIO_3 which separates is dissolved in 150 c.c. of hot water and the acid iodate $KH(IO_3)_2$ present is neutralised with KOH. On cooling pure KIO_3 separates.

Iodic acid, although monobasic, forms normal and acid salts :

Normal potassium iodate KIO_3
Acid potassium iodate KIO_3,HIO_3 or $KH(IO_3)_2$
Diacid potassium iodate $KIO_3,2HIO_3$ or $KH_2(IO_3)_3$.

The acid salts are isomorphous with acid salts of some dibasic organic acids (succinic, etc.). The freezing points of concentrated solutions of iodic acid suggest that $H_2I_2O_6$ is present. The normal iodates are sparingly soluble or insoluble in water. On heating they decompose (i) into iodide + oxygen, *e.g.* KIO_3 (no periodate is formed) ; (ii) into oxide + iodine + oxygen, *e.g.* $Ca(IO_3)_2$. Barium iodate forms a periodate (see below). Iodates form complex compounds with molybdic, tungstic, and phosphoric acids.

From a solution of KIO_3 in aqueous HF the **difluo-iodate** KIO_2F_2 crystallises, and from iodic acid in a solution of HF in glacial acetic acid $IOF_3,5H_2O$, which is probably $(HO)_2IF_3,4H_2O$, compounds of which with organic bases, *e.g.* $(HO)_2IF_3$,py, are known (Weinland, 1908).

Iodates give a blue colour, due to liberation of iodine, with starch paste and sulphurous acid. Mercurous nitrate precipitates yellow mercurous iodate $Hg_2(IO_3)_2$ and mercuric nitrate precipitates white mercuric iodate $Hg(IO_3)_2$, insoluble in dilute nitric acid (mercuric bromate is soluble) ; silver nitrate gives a white precipitate of silver iodate $AgIO_3$, insoluble in dilute nitric acid.

A soluble iodate may be determined by adding a solution of iodide and acidifying, the iodine liberated being titrated : $IO_3' + 5I' + 6H^{\cdot} = 3I_2 + 3H_2O$. A mixture of iodate and iodide may also be used to determine an acid ($H^{\cdot}$) by titrating the iodine liberated.

Periodic acid H_5IO_6 (the common form or **paraperiodic acid**), discovered by Ammermüller and Magnus in 1833, is formed by the electrolytic oxidation of iodic acid with a lead dioxide anode in a porous cell (Müller, 1901 ; Hickling and Richards, *J.C.S.*, 1940, 256).

A **periodate** is most conveniently made by oxidising an iodate in alkaline solution by chlorine :

$$IO_3' + Cl_2 + 3OH' = H_3IO_6'' + 2Cl',$$

and by heating with silver nitrate solution at 100° a black silver **periodate** Ag_3IO_5 is precipitated :

$$H_3IO_6'' + 3Ag^{\cdot} = Ag_3IO_5 + H_2O + H^{\cdot}.$$

When chlorine is passed into a suspension of this, a solution of **periodic acid** is formed, which gives H_5IO_6 when crystallised :

$$4Ag_3IO_5 + 6Cl_2 + 10H_2O = 4H_5IO_6 + 12AgCl + 3O_2.$$

A rapid stream of chlorine is passed into a boiling solution of 12·7 g. of iodine and 60 g. of sodium hydroxide in 600 c.c. of water, when a white precipitate of acid sodium periodate $Na_2H_3IO_6$ is formed :

$$NaIO_3 + 3NaOH + Cl_2 = Na_2H_3IO_6 + 2NaCl.$$

A suspension of this in water at 100° gives with silver nitrate a black precipitate of silver mesoperiodate Ag_3IO_5, which is suspended in water and decomposed by chlorine (avoiding excess). The solution of periodic acid is filtered from the silver chloride, concentrated on a water bath and kept in a vacuum desiccator over calcium chloride and then P_2O_5, when crystals of H_5IO_6 separate (Partington and Bahl, *J.C.S.*, 1934, 1086).

The colourless deliquescent monoclinic crystals of H_5IO_6 melt at 140° with decomposition, evolving ozonised oxygen : $2H_5IO_6 = 2HIO_3 + 4H_2O + O_2$.

By exposing H_5IO_6 at 80° in vacuum for several hours **dimesoperiodic acid** $H_4I_2O_9$ is formed, at 100° **metaperiodic acid** HIO_4 results, which does not lose water to form I_2O_7 but sublimes (Partington and Bahl, *J.C.S.*, 1934, 1088).

The periodic acids and periodates may be formally regarded as produced by successive addition of water to the *hypothetical* anhydride I_2O_7 :

Metaperiodic acid HIO_4 : $I_2O_7 + H_2O = 2HIO_4$. Salts are KIO_4, $AgIO_4$.
Dimesoperiodic acid $H_4I_2O_9$: $I_2O_7 + 2H_2O = H_4I_2O_9$. Salts are $Na_4I_2O_9$, $Ag_4I_2O_9$,
Mesoperiodic acid H_3IO_5 (unknown) : $I_2O_7 + 3H_2O = 2H_3IO_5$. Salts are Ag_3IO_5, $Pb_3(IO_5)_2$.
Paraperiodic acid H_5IO_6 (the common form) : $I_2O_7 + 5H_2O = 2H_5IO_6$. Salts are Ag_5IO_6, $Na_2H_3IO_6$, $Na_3H_2IO_6$, $Ba_5(IO_6)_2$.

Potassium iodate decomposes on heating without forming periodate : $2KIO_3 = 2KI + 3O_2$, but barium iodate forms a periodate stable at a red heat : $5Ba(IO_3)_2 = Ba_5(IO_6)_2 + 4I_2 + 9O_2$. The periodates are mostly sparingly soluble. Periodic acid and soluble periodates are powerful oxidising agents, converting manganous salts into permanganic acid, and in neutral or acid solution they liberate iodine from iodides : $IO_4' + 2I' + H_2O = IO_3' + I_2 + 2OH'$.

Silver nitrate with KIO_4 solution precipitates brown $AgIO_4$, soluble in dilute nitric acid : it is decomposed by hot water : $2AgIO_4 + 4H_2O = Ag_2H_3IO_6 + H_5IO_6$.

KIO_4 and $RbIO_4$ (tetragonal) are not isomorphous with $KClO_4$ (rhombic), which is isomorphous with $CsIO_4$. Complex acids are formed with periodic acid and tungstic and molybdic acids, and a fluorine substitution product is $CsIO_4,3CsIO_3F_2,5H_2O$.

Interhalogen Compounds

The halogens form compounds with one another (p. 762 ; *Ann. Rep. C.S.*, 1933, 128). Each one combines with all the other halogens.

Chlorine monofluoride ClF is a colourless gas formed from hydrogen fluoride and chlorine at liquid air temperature, or by heating fluorine and chlorine in a copper vessel at 250°. It reacts with some metals even more vigorously than

fluorine itself. Excess of fluorine forms gaseous **chlorine trifluoride** ClF_3 (b.p. 11·3°), which attacks glass very vigorously.

Bromine trifluoride BrF_3, formed from fluorine and bromine or hydrogen bromide, is a colourless fuming liquid; **bromine pentafluoride** BrF_5 is also a liquid, formed from the elements at 0°, the vapour being stable at 460°; **bromine monofluoride** BrF is a reddish-brown unstable liquid (b.p. *c.* 20°) formed from the trifluoride and bromine.

A liquid **iodine pentafluoride** IF_5 is formed by direct combination of the elements, by the action of fluorine on heated I_2O_5, or (Gore, 1871) by heating iodine with silver fluoride. When heated with fluorine at 270°–300° it forms the gaseous **iodine heptafluoride** IF_7, with the normal vapour density.

Bromine chloride BrCl has been detected by the absorption spectrum of a mixture of chlorine and bromine vapour, but the vapour pressure and freezing point curves show no indication of it. A solid hydrate $BrCl,4H_2O$ is formed by passing chlorine into bromine covered with water, and can be crystallised from solution up to 18° (Anwar-Ullah, *J.C.S.*, 1932, 1176).

Iodine chlorides.—The freezing point diagram (Fig. 333) of the iodine-chlorine system shows two compounds, ICl and ICl_3.

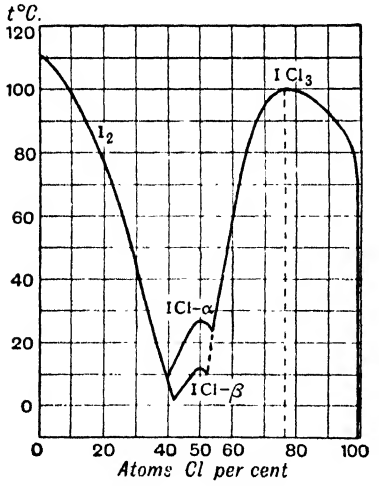


FIG. 333.—Chlorine-iodine system.

Iodine monochloride ICl is formed by passing chlorine over iodine as a dark red liquid which on standing (especially in contact with a trace of ICl_3) solidifies. It is also formed by heating iodine with potassium chlorate (Thorpe and Perry, *J.C.S.*, 1892, **61**, 925): $KClO_3 + I_2 = KIO_3 + ICl$, and by boiling iodine with aqua regia. There are two forms of the solid, a stable form in red needles, m.p. 27·2°, formed by strong and rapid cooling of the liquid, and a nearly black metastable form, m.p. 13·9°, obtained by slowly cooling the liquid below −10°, which is always metastable, there being no transition temperature. The vapour density is normal.

Iodine trichloride ICl_3 is formed by the action of excess of chlorine on iodine or iodine monochloride as a lemon-yellow or orange-red fuming crystalline solid. It dissociates completely on heating at 67°: $ICl_3 \rightleftharpoons ICl + Cl_2$, but melts in chlorine under pressure. It is also formed by heating iodine pentoxide in hydrogen chloride: $I_2O_5 + 10HCl = 2ICl_3 + 5H_2O + 2Cl_2$.

EXPT. 11.—A jar of hydrogen iodide is inverted over a jar of dry chlorine and the glass plates withdrawn. There is a violent reaction (sometimes a red flame) and violet iodine vapour is formed. On standing, three substances separate: (i) solid crystals of iodine in the upper jar, (ii) dark red drops of ICl

at the junction of the two jars, (iii) lemon-yellow crystals of ICl_3 in the lower jar. On standing (in presence of excess of chlorine) all is converted into yellow ICl_3. The reaction is : $4HI + 4Cl_2 = 4HCl + I_2 + ICl + ICl_3$.

Iodine monobromide IBr is formed in black crystals, like iodine, by direct combination. The vapour is dissociated (Yost, Anderson and Skoog, *J.A.C.S.*, 1933, **55**, 552).

Iodine monochloride dissolves in water with some decomposition :

$$5ICl + 3H_2O \rightleftharpoons 2I_2 + HIO_3 + 5HCl,$$

but in concentrated hydrochloric acid the reaction is reversed. Iodine trichloride is less soluble in water and is almost completely hydrolysed :

$$2ICl_3 + 3H_2O \rightleftharpoons ICl + HIO_3 + 5HCl ;$$

HOI and $I(OH)_3$ are supposed to be formed as intermediate stages. In dilute acid solution an iodate and iodide liberate iodine (p. 806) :

$$IO_3' + 5I' + 6H^{\cdot} = 3I_2 + 3H_2O,$$

but in presence of excess of concentrated hydrochloric acid an excess of iodate converts the iodine into iodine monochloride :

$$IO_3' + 2I_2 + 6HCl = Cl' + 5ICl + 3H_2O ;$$

hence the total reaction with iodate and iodide is :

$$IO_3' + 2I' + 6HCl = 3Cl' + 3ICl + 3H_2O.$$

An iodide may be titrated by adding concentrated hydrochloric acid and a drop of chloroform, and adding iodate solution till the purple colour of the solution of iodine in chloroform just disappears on shaking.

Iodine monochloride and iodine trichloride are decomposed by alkali hydroxide solutions giving iodates and iodides :

$$3ICl + 6OH' = 3Cl' + 2I' + IO_3' + 3H_2O$$
$$3ICl_3 + 12OH' = 9Cl' + I' + 2IO_3' + 6H_2O,$$

but iodine is liberated as an intermediate stage.

Iodine salts.—The tendency of iodine to function as a positive cation in the case of hypo-iodous acid (p. 812) : $HOI \rightleftharpoons OH' + I^{\cdot}$ is also found with iodine chlorides, which sometimes behave as if they were dissociating into iodine cations : $ICl \rightleftharpoons I^{\cdot} + Cl'$ and $ICl_3 \rightleftharpoons I^{\cdots} + 3Cl'$. Iodine salts with oxy-acids are also described, although some are doubtful.

Liquid iodine monochloride is a conductor, iodine migrating to the cathode and chlorine to the anode, hence the dissociation $ICl \rightleftharpoons I^{\cdot} + Cl'$ is assumed. Non-aqueous solutions of iodine trichloride are also conductors, and since the molecular weight in solution is only about half the normal value, a dissociation $ICl_3 \rightleftharpoons ICl_2^{\cdot} + Cl'$ is assumed.

The chlorides of iodine thus behave as salts of the positive ions $I^{\cdot}$ and $I^{\cdots}$, and oxysalts described are : $[I\,py_2]NO_3$, $[I\,py_2]ClO_4$ (py = pyridine) by Carlsohn (1935) ; **iodine acetate** $I(CH_3COO)_3$ formed by the action of Cl_2O on iodine

in glacial acetic acid; **iodine perchlorate** $I(ClO_4)_3$ formed in yellowish-green needles by the action of ozone on a cooled solution of iodine in anhydrous perchloric acid: $I_2 + 6HClO_4 + O_3 = 2I(ClO_4)_3 + 3H_2O$ (Fichter, 1928); **iodine orthophosphate** IPO_4 formed from iodine, orthophosphoric acid, acetic anhydride and fuming nitric acid; and the yellow **basic iodine sulphate** $(IO)_2SO_4$ formed from iodine and iodine pentoxide in concentrated sulphuric acid (Masson, *J.C.S.*, 1938, 1702). The strongly basic *diphenyliodonium hydroxide* $[(C_6H_5)_2I]OH$ is stable and forms salts like those of tervalent thallium, even to giving a green flame coloration.

The oxides I_4O_9 and IO_2 or I_2O_4 have also been regarded as an iodate $I(IO_3)_3$ and basic iodate $IO(IO_3)$, respectively, of tervalent iodine.

CHAPTER XXIX

MANGANESE AND RHENIUM

SUB-GROUP (*a*) of Group VII contains manganese and rhenium.

Element no. 43 was said to be detected by the X-ray spectrum by Noddack, etc., at the same time as rhenium and was called **masurium**, but although it is said to occur in minerals to about the same extent as rhenium no compounds of it have been isolated (*Ann. Rep. C.S.*, 1935, 143). A radioactive isotope is formed by bombarding molybdenum with deuterons (Perrier and Segrè, 1937) : $^{96}_{42}Mo + ^{2}_{1}D = ^{98}_{43}Ma$. It shows the properties of rhenium, except that it does not volatilise when heated in a current of HCl.

Sub-group (*a*) even series :	At. No.	Electron configuration	Density	At. Vol.	M. Pt.	B.Pt.
Mn - -	25	2·8·13·2	7·39	7·4	1260°	1900°
Re - -	75	2·8·18·32·13·2	21·2	8·7	3167°	—

The marked disparity in properties between members of the even and odd series which began in Group V and increased in Group VI has now reached an acute stage. The only property in which manganese and rhenium resemble the halogens is in the formation of volatile acidic heptoxides Mn_2O_7 and Re_2O_7, analogous to Cl_2O_7 (the corresponding oxides of the other halogens are unknown). Mn_2O_7 is explosive like Cl_2O_7, but Re_2O_7 is not. The perchlorates, *e.g.* $KClO_4$, and permanganates, *e.g.* $KMnO_4$, are isomorphous and both silver perchlorate and permanganate are sparingly soluble in water.

In its remaining compounds manganese as a transitional element shows close analogies with chromium and iron. The metals are similar in physical properties and both manganese and chromium form basic sesquioxides, dioxides, and acidic trioxides. Potassium chromate (yellow) K_2CrO_4 and potassium manganate (green) K_2MnO_4 are isomorphous. Manganese resembles Mg and Zn in forming a sparingly soluble $MnNH_4PO_4$. Manganese resembles iron in forming three oxides of the types MO, M_2O_3, and M_3O_4, the first two basic, although the sesquioxides are also weakly acidic. The manganous salts are more stable than the ferrous salts ; they do not oxidise in air and the sulphate is more stable to heat. The ferric and chromic compounds, on the other hand, are more stable than the manganic, *e.g.* $MnCl_3$ very easily decomposes into $MnCl_2$ and chlorine, and manganic salts are powerful oxidising agents. A manganese alum $KMn^{III}(SO_4)_2,12H_2O$ resembles ferric alum but is less stable. Manganic salts are easily hydrolysed since $Mn(OH)_3$ is a weak base and is amphoteric.

Manganese

The black native manganese dioxide MnO_2 (*pyrolusite*) is called by Pliny *magnes* and confused with magnetic oxide of iron Fe_3O_4. The name *pyrolusite* (Greek *pyr* fire, *luo* I wash) refers to the use of the mineral in decolorising

glass (p. 374). Pott in 1740 and Scheele in 1774 investigated pyrolusite; impure metallic manganese was first obtained by Gahn in 1774 by heating an oxide with carbon. A purer metal was obtained by John in 1807.

Pyrolusite MnO_2 occurs mainly in India, South Africa, the Gold Coast and Russia. It is usually contaminated with ferric oxide and barium, often in the form of *psilomelane* $(Mn,Ba)O,2MnO_2$ corresponding with Weldon mud $CaO,2MnO_2$. Most of the ore is used in smelting for ferro-manganese. Less important minerals are *braunite* Mn_2O_3, *hausmannite* Mn_3O_4, *manganite* Mn_2O_3,H_2O, the hydrated dioxides *wad* and *psilomelane*, *rhodocrosite* or *dialogite* $MnCO_3$, *rhodonite* $MnSiO_3$, *alabandite* MnS, and *hauerite* MnS_2. The deposits of hydrated oxides are sedimentary or metamorphic.

Manganese occurs in small amounts in some meteorites; manganese dioxide occurs with ferric oxide in nodules on the ocean bed; manganese compounds occur in the soil, and are important in biological processes (Godden, *J.S.C.I.*, 1939, **58**, 791).

Impure manganese, containing carbon, is obtained by strongly heating the oxide Mn_3O_4 with carbon: $Mn_3O_4 + 4C = 3Mn + 4CO$. With less than the theoretical amount of carbon in the electric furnace a metal nearly free from carbon is obtained, but it volatilises readily at the high temperature (b.p. 1900°). A purer metal is obtained by the aluminothermic process (p. 738):

$$3Mn_3O_4 + 8Al = 9Mn + 4Al_2O_3.$$

Pure manganese is obtained by electro-deposition from an acidified solution of manganous and ammonium sulphates and heating in vacuum to remove hydrogen (this metal does not decompose water), or by the electrolysis of concentrated manganous chloride solution with a mercury cathode and distilling off the mercury by heating the amalgam in vacuum at 250°.

Manganese is greyish- or reddish-white, hard and brittle, and with a fairly high m.p. (1260°). It is paramagnetic. Manganese is not easily oxidised in air unless it contains carbon or is finely divided (when it is pyrophoric), but (unless quite pure) it decomposes cold water with evolution of hydrogen and readily dissolves in dilute acids evolving hydrogen (even with cold dilute nitric acid: Campbell, *J.C.S.*, 1923, **123**, 2323) and forming manganous salts: $Mn + 2H^+ = Mn^{++} + H_2$. It combines with nitrogen above 1210° and with carbon in the electric furnace.

There are three allotropic forms of manganese, each with an unusual lattice. In α-Mn there are four kinds of manganese atoms, in β-Mn two types, and the structure of γ-Mn is formed from cubic close packing by shortening one edge of the unit cube.

Alloys of iron and manganese obtained in the blast furnace are *ferromanganese* (70–80 p.c. Mn and less than 0·3 p.c. carbon, for open-hearth steel) and *spiegeleisen* (20–32 p.c. Mn and more than 0·3 p.c. carbon, for Bessemer steel); *manganese steel* may contain up to 13 p.c. of Mn, is very hard and tough and is used for the jaws of rock-crushers and for machinery. Franklinite (p. 383) contains manganese and the residue in the zinc retorts is used to make ferromanganese. *Manganese bronze* is copper with variable amounts of manganese and zinc.

Alloys of copper and zinc with small quantities of manganese resemble German silver. *Manganin* is an alloy of copper, manganese and nickel, used for resistance coils since its electrical resistance is only slightly affected by temperature after it has been heated repeatedly at 120°. An alloy of copper, aluminium and manganese (*Heusler's alloy*) is ferromagnetic. Pure manganese becomes appreciably magnetic only on heating.

MANGANESE COMPOUNDS

1. A compound of *univalent manganese* is $Na_5[Mn^I(CN)_6]$ (p. 832).

2. Compounds of 2-*valent* manganese are the basic *monoxide* MnO and the *manganous salts, e.g.* $MnCl_2$ and $MnSO_4$.

3. Compounds of 3-*valent* manganese are the weakly acidic *sesquioxide* Mn_2O_3, forming *manganites* $M^I(Mn^{III}O_2)$, and the *manganic compounds, e.g.* $MnCl_3$ and $Mn_2(SO_4)_3$.

4. Compounds of 4-*valent* manganese are the *dioxide* MnO_2, acidic and forming *permanganites* $M_2^I(Mn^{IV}O_3)$, and compounds such as $Mn(SO_4)_2$.

5. Compounds of 6-*valent* manganese are the *manganates* $M_2^IMn^{VI}O_4$, isomorphous with sulphates.

6. Compounds of 7-*valent* manganese are the *heptoxide* Mn_2O_7, acidic and forming *permanganates* $M^IMn^{VII}O_4$, isomorphous with perchlorates.

The electronic structure of the manganese atom is : $2|2\cdot2\cdot4|2\cdot2\cdot4\cdot5|2$, total 25, the third quantum group containing 13 electrons. The loss of the two 4-quantum electrons gives the Mn^{++} ion. The other ions of different valency, including anions (manganate and permanganate ions) are formed by the 3-quantum electrons becoming 4-quantum valency electrons :

Mn^+	$2\|2\cdot2\cdot4\|2\cdot2\cdot4\cdot5\|1$	total 24	valency 1
Mn^{++}	$2\|2\cdot2\cdot4\|2\cdot2\cdot4\cdot5\|$	,, 23	,, 2
Mn^{+++}	$2\|2\cdot2\cdot4\|2\cdot2\cdot4\cdot4\|$	,, 22	,, 3
MnO_4^{--}	$2\|2\cdot2\cdot4\|2\cdot2\cdot4\cdot1\|6$ (2)	,, 27	,, 6
MnO_4^-	$2\|2\cdot2\cdot4\|2\cdot2\cdot4\|7$ (1)	,, 26	,, 7

The numbers in brackets ( ) denote the electrons gained from hydrogen or metal atoms, which become cations. Some of the oxygens are usually assumed to be attached by coordinate links, 2 in MnO_4'' and 3 in MnO_4' :

but the Mn to O distance in the tetrahedral MnO_4' ion of $KMnO_4$ is 1·49 A. (Mooney, *Phys. Rev.*, 1931, **37**, 1306), which corresponds with considerable double bond character, as it is similar to the distance in SO_4'' (1·51 A.) and ClO_4' (1·48 A.).

MANGANOUS SALTS

The soluble manganous salts MnX_2 are white or pale pink and give pink solutions containing the *manganous ion*, probably hydrated, $[Mn(H_2O)_4]^{..}$, also present in the crystal hydrates, which (unlike chromous and ferrous ions) shows practically no tendency to oxidise to higher valency. The hydroxide $Mn(OH)_2$,

however, is very easily oxidised by atmospheric oxygen to manganic hydroxide $Mn(OH)_3$ or $MnO(OH)$: $4Mn(OH)_2 + O_2 = 4MnO(OH) + 2H_2O$.

Manganous fluoride MnF_2, a white powder or red tetragonal crystals, is obtained by heating at 300° in carbon dioxide the white precipitate of $(NH_4)MnF_3$ formed by the action of a large excess of ammonium fluoride solution on a solution of manganous chloride (Nuka, 1929). It is sparingly soluble but forms a hydrate with $4H_2O$. Unlike the other manganous halides it is hydrolysed in solution.

Manganous chloride $MnCl_2$ is formed by the action of chlorine on manganese, but is usually prepared from pyrolusite. This is washed with dilute nitric acid to remove alkaline earth carbonates, dried, and heated in a crucible with half its weight of ammonium chloride ; the residue is extracted with boiling water and the solution crystallised :

$$3MnO_2 + 6NH_4Cl = 3MnCl_2 + N_2 + 4NH_3 + 6H_2O.$$

It is also obtained from the residue in the preparation of chlorine (p. 772) : $MnO_2 + 4HCl = MnCl_2 + Cl_2 + 2H_2O$. The solution usually contains ferric chloride which is precipitated by boiling with precipitated manganous carbonate : $2FeCl_3 + 3MnCO_3 + 3H_2O = 2Fe(OH)_3 + 3MnCl_2 + 3CO_2$; the filtrate is evaporated and the pink monoclinic $MnCl_2,4H_2O$ crystallises.

The rose-red anhydrous $MnCl_2$ (hexagonal) is formed on heating the dihydrate at 198° ; m.p. 650°, b.p. 1190°, the vapour density being normal. It forms a *green* solution in alcohol and combines with 1, 2 and $6NH_3$. Manganous chloride gives a green flame coloration.

The solubility curve shows hydrates with $6H_2O$ (− 37° to − 2°), $4H_2O$ (− 2° to 57·85°, two monoclinic forms), $2H_2O$ (58·089°). The ordinary form of $MnCl_2,4H_2O$ melts at 58·089° to solid $MnCl_2,2H_2O$ and saturated solution, and at 198° $MnCl_2,2H_2O$ forms $MnCl_2$.

Manganous bromide $MnBr_2$, rose-red, is obtained anhydrous (hexagonal) by adding bromine to powdered manganese covered with ether and heating at 100°. It forms pink $MnBr_2,4H_2O$ (monoclinic) and combines with 1, 2 and $6NH_3$. **Manganous iodide** MnI_2 is yellowish-brown or pink (hexagonal) and is formed on dehydrating the rose-red $MnI_2,4H_2O$ (monoclinic) in vacuum at room temperature ; it combines with 4, 6 and $9H_2O$ and with 2 and $6NH_3$. The hydrates of $MnBr_2$ and MnI_2 are formed by dissolving $MnCO_3$ in the acids and crystallising.

Manganous oxide MnO is a greyish-green powder formed by heating manganous carbonate or any higher oxide of manganese strongly in hydrogen ; if the hydrogen contains a trace of hydrogen chloride emerald-green cubic crystals of MnO are formed. MnO is also formed on heating manganous oxalate : $MnC_2O_4 = MnO + CO + CO_2$. It is reduced by hydrogen or carbon only at very high temperatures.

Manganous hydroxide $Mn(OH)_2$ occurs native as *pyrochroite* isomorphous with brucite (p. 365), and is formed as a white precipitate (solubility $4{\cdot}5 \times 10^{-4}$ mol/lit.) by adding alkali hydroxide to manganous chloride or sulphate solution. It rapidly absorbs atmospheric oxygen to form brown manganic hydroxide $MnO(OH)$. Colourless hexagonal crystals of $Mn(OH)_2$ are deposited on cool-

ing a boiling concentrated solution of potassium hydroxide to which manganous chloride is added, with exclusion of air.

Ammonia precipitates manganous hydroxide incompletely and the solution rapidly deposits manganic hydroxide on exposure to air. In presence of ammonium chloride only half the manganese is precipitated :

$$2MnCl_2 + 2NH_4OH = Mn(OH)_2 + (NH_4)_2MnCl_4.$$

Manganous borate $MnH_4(BO_3)_2$ is formed as an almost white powder by precipitating manganous sulphate or chloride solution with borax and drying at 100°. It is used as a *drier* for linseed oil, paints and varnishes : it acts catalytically, probably by the intermediate formation of a higher oxide.

Manganese compounds give an amethyst-coloured borax bead (Bancroft and Nugent, *J. Phys. Chem.*, 1929, **33**, 481).

Manganous carbonate $MnCO_3$ occurs native as the bright red *rhodocrosite* or *manganese spar*, rhombohedral and isomorphous with calcite, and as *mangano-calcite* $(Mn,Ca,Mg)CO_3$. It is formed as a white or pale buff-coloured precipitate on adding alkali carbonate to a manganous salt solution. It is decomposed by heat to manganous oxide : $MnCO_3 = MnO + CO_2$; at higher temperatures in air higher oxides are formed : $3MnO + CO_2 = Mn_3O_4 + CO$, and $4MnO + O_2 = 2Mn_2O_3$. Manganous carbonate is only sparingly soluble in water containing carbon dioxide, forming a bicarbonate. On exposure to air the solution deposits brown manganic hydroxide :

$$4Mn(HCO_3)_2 + 2H_2O + O_2 = 4Mn(OH)_3 + 8CO_2.$$

Manganous oxalate $MnC_2O_4,2H_2O$ is obtained as a white crystalline (octahedral) precipitate. It loses water at 100°–120° and at higher temperatures forms manganous oxide (*q.v.*).

Manganous nitrate is formed in solution by dissolving manganous carbonate in a slight excess of dilute nitric acid or boiling manganese dioxide with dilute nitric acid containing oxalic acid or sugar. On evaporation pink deliquescent monoclinic crystals of $Mn(NO_3)_2,6H_2O$, also soluble in alcohol, are obtained. The crystals decompose on heating : $Mn(NO_3)_2 = MnO_2 + 2NO_2$. The monohydrate is deposited on evaporating with concentrated nitric acid, and the anhydrous salt is obtained from this by warming with concentrated nitric acid and N_2O_5, or very slowly by dehydrating at room temperature over P_2O_5. $Mn(NO_3)_2$ forms hydrates with 6, 4, 2, $1\frac{1}{2}$, 1 and $\frac{1}{2}H_2O$ (Ewing and Glick, *J.A.C.S.*, 1940, **62**, 2174).

Manganous nitrate forms a series of double salts with bismuth and rare earth nitrates, with the formula $2M^{III}(NO_3)_3,3Mn(NO_3)_2,24H_2O$, which may be complex : $[Mn_3[M^{III}(NO_3)_6]_2,24H_2O$. (Mg, Zn, Co, etc., may replace Mn.)

Manganous phosphate $Mn_3(PO_4)_2,7H_2O$ is formed as a white amorphous precipitate on adding excess of Na_2HPO_4 to a manganous salt solution. In presence of ammonium chloride and ammonia a reddish-white glittering crystalline precipitate of **manganous ammonium phosphate** $MnNH_4PO_4,H_2O$ is formed. On heating to redness it forms **manganous pyrophosphate** $Mn_2P_2O_7$.

Manganous sulphide MnS occurs in cubic crystals as *alabandite*. It is formed as a grey mass by heating manganous carbonate with sulphur, or the oxide, carbonate, precipitated sulphide, or sulphate in hydrogen sulphide, or as a light flesh-coloured precipitate by ammonium chloride, ammonia and ammonium sulphide from a manganous salt solution. The precipitate dissolves in dilute acids, even acetic (in which zinc sulphide is insoluble). In contact with excess of ammonium sulphide or on heating in hydrogen sulphide at 320° it passes into a green crystalline form (Olsen and Rapalje, *J.A.C.S.*, 1904, **26**, 1613).

Sodium sulphide only slowly converts the pink to the green form. The X-ray spectra show that the green form is cubic (tetrahedral) and identical with alabandite. The rose-red form exists in two varieties, a hexagonal (wurtzite type), precipitated by sodium sulphide, and a cubic, precipitated by ammonium sulphide. The flesh-coloured precipitate is a mixture of the green and red cubic forms (Weiser and Milligan, *J. Phys. Chem.*, 1931, **35**, 2330; 1932, **36**, 2840; Schnaase, *Z. phys. Chem.*, 1933, **20B**, 89).

The **disulphide** MnS_2, occurring as *hauerite*, and formed by heating a solution of $MnCl_2$ and alkali polysulphide in a sealed tube, probably contains bivalent Mn but its structure is quite different from that of iron pyrites (p. 853), the Mn to S distance 2·59 A. being very large, so that the bonds are probably largely ionic. The selenide $MnSe_2$ and telluride $MnTe_2$ are similar (Elliott, *J.A.C.S.*, 1937, **59**, 1958).

Manganous sulphate $MnSO_4$ can be prepared from pyrolusite by heating with concentrated sulphuric acid: $2MnO_2 + 2H_2SO_4 = 2MnSO_4 + 2H_2O + O_2$, evaporating, heating the residue to decompose ferric sulphate (as impurity): $Fe_2(SO_4)_3 = Fe_2O_3 + 3SO_3$, dissolving, filtering and evaporating, when pink efflorescent monoclinic or rhombic crystals of $MnSO_4,4H_2O$ separate. The last trace of iron may be precipitated by boiling the solution with a little precipitated manganous carbonate.

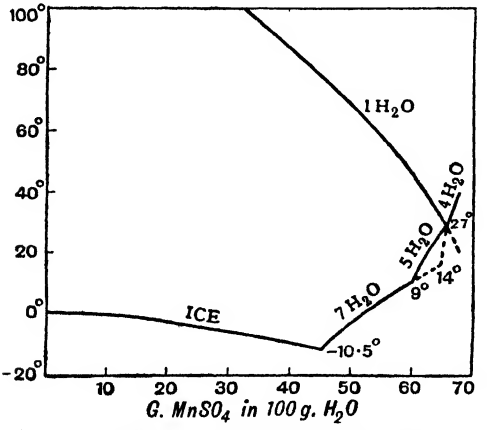


FIG. 334.—Manganous sulphate-water system.

The solubility curve (Fig. 334) shows several hydrates: $MnSO_4,7H_2O$ (monoclinic, isomorphous with $FeSO_4,7H_2O$) below 9°; between 9° and 27° $MnSO_4,5H_2O$ (triclinic, isomorphous with $CuSO_4,5H_2O$); above 27° (when the solubility is a maximum) $MnSO_4,H_2O$ (monoclinic, occurring as *szmikite*). The common crystalline salt is $MnSO_4,4H_2O$, separating as a labile form in a restricted temperature interval about 26°, with a transition temperature at 14°

between the 7 and $4H_2O$ forms. On heating at 280° almost white anhydrous $MnSO_4$ (m.p. 700°, decomp. 850°) is formed. Well-crystallised double salts are $K_2Mn(SO_4)_2,6H_2O$ and $(NH_4)_2Mn(SO_4)_2,6H_2O$ (monoclinic, isomorphous with ferrous ammonium sulphate), and $MnAl_2(SO_4)_4,22H_2O$ is the mineral *apjohnite*. A pink crystalline **basic sulphate** $MnO,2MnSO_4,3H_2O$ is formed by adding dilute KOH to boiling 25 p.c. $MnSO_4$ solution and boiling for some time, and an **acid sulphate** $MnH_2(SO_4)_2$ by crystallising from concentrated sulphuric acid.

Manganic Compounds

Except the oxide Mn_2O_3 the tervalent manganese compounds are much less stable than the bivalent. They are mostly covalent, and in solution either form complex ions (*e.g.* $MnCl_5''$) or tend to hydrolyse to a brown precipitate of manganic hydroxide MnO(OH), and are thus less stable than the chromic and ferric compounds they otherwise resemble.

Manganic oxide Mn_2O_3 occurs native as *braunite* (cubic) and hydrated as *manganite* MnO(OH) (rhombic). It is a brown powder formed by heating MnO or MnO_2 to redness in air (Drucker and Hüttner, *Z. phys. Chem.*, 1927, **131**, 237). It dissolves completely in dilute hydrofluoric or hydrocyanic acid forming complex compounds of 3-valent manganese, and in concentrated sulphuric and phosphoric acids forming manganic compounds. These reactions, and its magnetic susceptibility (Bhatnagar, etc., *J.C.S.*, 1939, 1433), show that it is a true manganic compound and its formula is O=Mn—O—Mn=O. With hot dilute nitric acid the oxide and hydroxide give manganous nitrate and manganese dioxide: $Mn_2O_3 + 2HNO_3 = Mn(NO_3)_2 + MnO_2 + H_2O$.

Manganic hydroxide MnO(OH) is formed as a brown powder by passing chlorine into a suspension of manganous carbonate in water or sodium carbonate solution and dissolving out the excess of manganous carbonate by very dilute nitric acid (Carius, *Annalen*, 1856, **98**, 53):

$$3MnCO_3 + Cl_2 + H_2O = 2MnO(OH) + MnCl_2 + 3CO_2.$$

Mangano-manganic oxide (*red oxide of manganese*) Mn_3O_4 occurs native as tetragonal *hausmannite*. It is formed by *strongly* heating manganese dioxide out of contact with air: $3MnO_2 = Mn_3O_4 + O_2$ (at a lower temperature Mn_2O_3 is formed), or at 940° in air or 1090° in oxygen. It slowly dissolves in cold concentrated sulphuric acid to a red solution of manganous and manganic sulphates: $Mn_3O_4 + 4H_2SO_4 = MnSO_4 + Mn_2(SO_4)_3 + 4H_2O$, and thus behaves like manganous manganite MnO,Mn_2O_3 or $Mn^{II}(Mn^{III}O_2)_2$. Boiling dilute nitric acid forms manganous nitrate and manganese dioxide: $Mn_3O_4 + 4HNO_3 = 2Mn(NO_3)_2 + MnO_2 + 2H_2O$, so that it has been formulated as basic manganous permanganite $2MnO,MnO_2$ or $Mn_2^{II}O(Mn^{IV}O_3)$, but this is inconclusive, as Mn_2O_3 behaves similarly (see above).

Manganic fluoride $MnF_3,3H_2O$ is formed in deep red crystals by dissolving Mn_2O_3 in hydrofluoric acid and by the action of permanganate or manganese dioxide on a manganous salt in hydrofluoric acid: $MnO_4' + 4Mn'' + 8H' = 5Mn''' + 4H_2O$, and $MnO_2 + Mn'' + 4H' = 2Mn''' + 2H_2O$. It forms complex salts, *e.g.*

K_2MnF_5,H_2O, and there is a thallium salt formulated as $2MnF_3,MnF_2,5TlF$, or $Mn^{II}Tl_5[Mn_2^{III}F_{13}]$. Anhydrous MnF_3 is obtained by the action of fluorine on manganous iodide.

Manganic chloride or **manganese trichloride** $MnCl_3$ is present (probably as the complex ion $MnCl_5''$) in the deep red or brown solution of manganese dioxide in cold concentrated hydrochloric acid :

$$2MnO_2 + 8HCl = 2MnCl_3 + 4H_2O + Cl_2,$$

which decomposes on heating : $2MnCl_3 = 2MnCl_2 + Cl_2$. When poured into water the solution on standing deposits manganese dioxide :

$$2MnCl_3 + 2H_2O = MnO_2 + MnCl_2 + 4HCl.$$

A complex salt K_2MnCl_5 is formed by saturating the brown solution with hydrogen chloride gas and adding solid potassium chloride (Rice, *J.C.S.*, 1898, **73**, 258 ; Meyer and Best, *Z. anorg. Chem.*, 1899, **22**, 169).

A solid containing $MnCl_3$ is formed by passing hydrogen chloride into a suspension of manganese dioxide in carbon tetrachloride (Holmes, *J.A.C.S.*, 1907, **29**, 1277 ; 1908, **30**, 1192), and brown solid $MnCl_3$, stable below $-35°$ but decomposing at higher temperatures into $MnCl_2$ and chlorine, is formed by the action of anhydrous hydrogen chloride on anhydrous manganic acetate $Mn(CH_3COO)_3$, prepared by heating $Mn(NO_3)_2,2H_2O$ with acetic anhydride (Varga, *Bull. Soc. Chim.*, 1936, **3**, 2385).

Manganic phosphate $MnPO_4,H_2O$ is formed as a greenish-grey precipitate when a solution of manganous sulphate containing acetic and phosphoric acids is oxidised by potassium permanganate at 100°. It is insoluble in water but forms violet solutions in concentrated sulphuric and phosphoric acids. A violet solution and a lilac precipitate of **acid manganic pyrophosphate** $MnHP_2O_7$ are formed by heating a manganous salt with a mixture of phosphoric and nitric acids. Manganese salts give a violet microcosmic salt bead.

Manganic sulphate $Mn_2(SO_4)_3$ is formed as a dark green powder by heating precipitated MnO_2 with concentrated sulphuric acid at 138°, draining on a porous tile, washing with concentrated nitric acid and drying at 130° (Carius, 1856). It dissolves in water to a violet liquid which deposits brown MnO(OH) on dilution. It forms *alums* isomorphous with common alum. $KMn(SO_4)_2,12H_2O$ and $(NH_4)Mn(SO_4)_2,12H_2O$ form violet octahedral crystals, hydrolysed by water to MnO(OH) and hence difficult to obtain pure, but $RbMn(SO_4)_2,12H_2O$ and especially the ruby-red $CsMn(SO_4)_2,12H_2O$ are stable and crystallise well : the Cs alum is formed by electrolytic oxidation of a solution of $MnSO_4$ and Cs_2SO_4 in 1 : 3 sulphuric acid (Piccini, 1899). **Acid manganic sulphate** $HMn(SO_4)_2,2H_2O$ is formed in dark red crystals from a solution of $KMnO_4$ in concentrated sulphuric acid at 70° (see Mn_2O_7).

Quadrivalent Manganese

The most familiar compound of 4-valent manganese is **manganese dioxide**, the structure O=Mn=O of which is confirmed by the magnetic susceptibility (Bhatnagar, etc., *J.C.S.*, 1939, 1433). It occurs native as rhombic (perhaps

pseudomorphic) *pyrolusite* and rarely as tetragonal *polianite* with a rutile lattice (p. 244) isomorphous with cassiterite SnO_2 and zirconia ZrO_2. *Pure* manganese dioxide is not easily prepared; Gorgeu (1890) obtained it as a lustrous black solid by heating 600 g. of manganous nitrate till red fumes appear, decanting the clear liquid from lower oxides and heating it for 40–60 hours at 150°–160°: $Mn(NO_3)_2 = MnO_2 + 2NO_2$. Lower oxides are removed by dilute nitric acid. Oxidising agents such as $KMnO_4$, NaOCl, ozone, or bromine and ammonia, give with manganous salts brown precipitates containing less oxygen than MnO_2, probably because compounds of MnO_2 and MnO are formed.

Manganese dioxide is acidic and with strong bases forms **permanganites** (often called *manganites*, which are properly compounds of Mn_2O_3), *e.g.* CaO,MnO_2 or $CaMnO_3$ and Weldon mud (p. 772), $CaO,2MnO_2$ or $CaMn_2O_5$, but many of these are doubtful. A colloidal solution of MnO_2 is formed by the action of ammonia on boiling permanganate solution.

Besides its use in decolorising glass (p. 374), manganese dioxide is used (with ferric oxide) in forming a dark brown glaze on pottery, and as a depolariser in the Leclanché cell, when it is reduced to Mn_2O_3 (Thompson, *T. Amer. Electrochem. Soc.*, 1935, **68**, 81); it is a conductor of electricity.

Manganese tetrafluoride MnF_4 is known only in complex salts such as K_2MnF_6 formed in small yellow tablets from a solution of potassium permanganate in 40 p.c. hydrofluoric acid; it is hydrolysed by water (rapidly on heating) with deposition of manganese dioxide (Weinland and Lauenstein, 1899).

Manganese tetrachloride is supposed to be present in the dark red or brown solution of manganese dioxide in cold concentrated hydrochloric acid (Vernon, *Proc. C.S.*, 1890, **6**, 58; *Phil. Mag.*, 1891, **31**, 469; Campbell, *J.C.S.*, 1923, **123**, 892) but has not been obtained in the solid state. The solution may contain the ion $MnCl_6''$: $MnO_2 + 6HCl = MnCl_6'' + 2H^{\cdot} + 2H_2O$.

A black crystalline complex salt K_2MnCl_6 is precipitated on boiling potassium permanganate with glacial acetic acid and saturating the reddish-brown solution with hydrogen chloride (Meyer and Best, 1899); it is also precipitated by the action of 40 p.c. hydrochloric acid and potassium chloride solution on calcium permanganate in a freezing mixture, and there are similar rubidium and ammonium salts (Weinland and Dinkelacker, 1908).

Manganese disulphate $Mn(SO_4)_2$ is formed as a brown solution, which is a powerful oxidising agent, by electrolytic oxidation of a solution of $MnSO_4$ in fairly concentrated sulphuric acid. It is hydrolysed by water.

MANGANATES

The formation of a green mass, giving a green solution with water which turned red on dilution was noticed by Glauber (1659) and Scheele (1774), who called it *mineral chameleon*, but the formulae of the manganates and permanganates were first established by Mitscherlich in 1832.

The green **manganates** are derived from an unknown trioxide MnO_3 containing 6-valent Mn. They are very stable and powerful oxidising agents. When

acidified they form permanganates (containing 7-valent Mn) and manganese dioxide :

$$3Mn^{VI} = 2Mn^{VII} + Mn^{IV} \text{ or } 3Mn^{VI}O_4'' + 4H^{\cdot} = 2Mn^{VII}O_4' + Mn^{IV}O_2 + 2H_2O.$$

Manganic acid H_2MnO_4 is, therefore, unknown even in solution.

Although manganese trioxide MnO_3 was said (Thorpe and Hambly, *J.C.S.*, 1883, **53**, 175) to be formed by dropping a green solution of potassium permanganate in concentrated sulphuric acid on sodium bicarbonate, the purple fumes evolved are droplets of permanganic acid (Lankshear, *Proc. C.S.*, 1912, **28**, 198 ; *Z. anorg. Chem.*, 1913, **82**, 97).

When manganese dioxide is fused with potassium or sodium hydroxide with free exposure to air a green mass of manganate is formed :

$$2Mn^{IV}O_2 + 4OH' + O_2 = 2Mn^{VI}O_4'' + 2H_2O$$
$$2MnO_2 + 4KOH + O_2 = 2K_2MnO_4 + 2H_2O.$$

The reaction is more complete with KOH (2 mols to 1 mol of MnO_2 : Schlesinger, etc., *Ind. Eng. Chem.*, 1919, **11**, 317 ; 1923, **15**, 53) and takes place more rapidly if potassium chlorate or nitrate is added :

$$MnO_2 + 2KOH + KNO_3 = K_2MnO_4 + KNO_2 + H_2O$$
$$3MnO_2 + 6KOH + KClO_3 = 3K_2MnO_4 + KCl + 3H_2O.$$

The cooled dark green mass dissolves in a *small* amount of cold water to a dark green solution which on evaporation in vacuum deposits dark green crystals of manganate, K_2MnO_4 or $Na_2MnO_4,10H_2O$, isomorphous with the corresponding sulphates. Crude sodium manganate is used as a disinfectant.

A manganate is formed by boiling a permanganate with very concentrated alkali hydroxide :

$$4Mn^{VII}O_4' + 4OH' = 4Mn^{VI}O_4'' + O_2 + 2H_2O.$$

EXPT. 1.—Boil 10 g. of $KMnO_4$ with 30 g. of KOH in 50 c.c. of water in a flask to about half the volume, when the colour becomes pure dark green. Add 25 c.c. of water, cool in ice, filter the K_2MnO_4 by suction in a sintered glass filter and dry over P_2O_5 in a desiccator.

Barium manganate $BaMnO_4$ forms a violet-black precipitate on adding a barium salt to an alkaline manganate solution. Strontium salts give a green precipitate of a basic strontium manganic manganate $MnO_2,MnO_3,3SrO,H_2O$ and a red solution of permanganate (Auger and Billy, 1902).

The dark green manganate solution is stable in presence of excess of alkali. On dilution it deposits manganese dioxide and gives a purple solution of permanganate :

$$3Mn^{VI}O_4'' + 2H_2O = 2Mn^{VII}O_4' + Mn^{IV}O_2 + 4OH',$$

and this occurs more readily on acidification or by passing carbon dioxide into the solution :

$$3Mn^{VI}O_4'' + 4H^{\cdot} = 2Mn^{VII}O_4' + Mn^{IV}O_2 + 2H_2O$$
$$3Mn^{VI}O_4'' + 2H_2O + 4CO_2 = 2Mn^{VII}O_4' + Mn^{IV}O_2 + 4HCO_3'.$$

Permanganate is formed without precipitation of manganese dioxide on passing chlorine into the manganate solution :

$$2MnO_4'' + Cl_2 = 2MnO_4' + 2Cl',$$

or by electrolytic oxidation with a nickel anode in a divided cell :

$$2MnO_4'' + O + H_2O = 2MnO_4' + 2OH'.$$

PERMANGANATES

The **permanganates** containing the ion $Mn^{VII}O_4'$ of 7-valent manganese are salts of **permanganic acid** $HMnO_4$, which is known in solution and its anhydride **manganese heptoxide** Mn_2O_7 in the pure state. They are all very powerful oxidising agents. Permanganates are isomorphous with perchlorates, containing 7-valent chlorine (p. 763).

Manganese heptoxide.—When powdered potassium permanganate is added in small portions to cooled concentrated sulphuric acid, a dark green solution (perhaps containing $(MnO_3)_2SO_4$) is formed which is liable to explode violently in contact with traces of organic matter or even spontaneously, and should never be prepared in quantity. When ice-cold water is cautiously added, dark brown drops of manganese heptoxide separate :

$$2KMnO_4 + 2H_2SO_4 = 2KHSO_4 + Mn_2O_7 + H_2O.$$

Manganese heptoxide was noticed by Chevillot and Edwards in 1837; its formula was determined by Aschoff in 1860. It is an opaque oily liquid, s. g. 2·4, which forms a violet vapour at 40°–50° but *explodes violently* on warming or in presence of organic matter. With water it forms a violet solution of $HMnO_4$, with some decomposition. It dissolves unchanged in glacial acetic acid.

Permanganic acid $HMnO_4$ is formed as a purple solution on adding dilute manganous sulphate or nitrate solution to boiling dilute nitric acid and lead dioxide :

$$2MnSO_4 + 5PbO_2 + 6HNO_3 = 2HMnO_4 + 2PbSO_4 + 3Pb(NO_3)_2 + 2H_2O,$$

or by oxidising a manganous salt in cold dilute nitric acid by sodium bismuthate (p. 642) :

$$2Mn(NO_3)_2 + 5NaBiO_3 + 16HNO_3 = 2HMnO_4 + 5NaNO_3 + 5Bi(NO_3)_3 + 7H_2O.$$

By precipitating a solution of potassium permanganate with hydrofluosilicic acid : $2KMnO_4 + H_2SiF_6 = K_2SiF_6 + 2HMnO_4$, or a solution of barium permanganate with dilute sulphuric acid, a purple solution of permanganic acid is formed, which is stable when dilute and may be concentrated in vacuum to 20 p.c. It is a strong monobasic acid and a powerful oxidising agent. Concentrated solutions evolve oxygen and deposit manganese dioxide :

$$4HMnO_4 = 4MnO_2 + 2H_2O + 3O_2.$$

When shaken with hydrogen or carbon monoxide the gas is absorbed and oxygen evolved.

On adding sodium chloride to the green solution of potassium permanganate in concentrated sulphuric acid, a yellow gas is evolved which condenses in a freezing mixture to a greenish-brown liquid said to be **permanganyl chloride** MnO_3Cl (Dumas, 1827). It explodes on heating and in moist air emits purple fumes, owing to hydrolysis. **Permanganyl fluoride** MnO_3F is said to be formed on adding calcium fluoride to the solution of $KMnO_4$ in concentrated sulphuric acid (Wöhler, 1827). The substances were not analysed.

Potassium permanganate is obtained by the action of acid, carbon dioxide or chlorine on a solution of potassium manganate, or by its electrolytic oxidation, as explained above. It crystallises easily and can be obtained pure.

EXPT. 2.—A powdered mixture of 50 g. of potassium hydroxide and 25 g. of potassium chlorate is fused on one iron sand-bath covered with another, and 50 g. of finely powdered pyrolusite gradually stirred in with an iron rod. Heating is continued until the mass stiffens: it is cooled, extracted with 1 lit. of water, boiled and carbon dioxide passed in until a drop of the liquid on filter paper gives a purple colour (no green). The liquid is allowed to settle, filtered through asbestos, evaporated to 300 c.c. and filtered hot through asbestos. On cooling potassium permanganate crystallises. A further crop is obtained by evaporating the mother-liquor to 100 c.c. and cooling.

Potassium permanganate forms deep purple-red brilliant rhombic prisms, with a green iridescence, which becomes dull in air owing to superficial reduction. It dissolves in water (4·4 in 100 at 10°; 5·31 at 15°; 32·4 at 75°) to a deep purple solution, which is opaque unless quite dilute. The formula $KMnO_4$ (not $K_2Mn_2O_8$) is found from the conductivity by Ostwald's rule (p. 149). The crystals at 240° evolve oxygen and fall to a black powder:

$$2KMnO_4 = K_2MnO_4 + MnO_2 + O_2.$$

At a red heat the manganate is decomposed to oxygen and permanganite:

$$2K_2MnO_4 = 2K_2MnO_3 + O_2.$$

Sodium permanganate $NaMnO_4$, or $NaMnO_4,3H_2O$, does not crystallise easily; its solution is used as a disinfectant (*Condy's fluid*). **Calcium permanganate** $Ca(MnO_4)_2$ is a deep violet hygroscopic and very soluble powder which loses oxygen more easily than the potassium salt. **Barium permanganate** $Ba(MnO_4)_2$, used in making permanganic acid, is best made as follows (Muthmann, 1893).

A solution of potassium permanganate, barium nitrate and barium hydroxide is boiled, when oxygen is evolved and a precipitate of barium manganate $BaMnO_4$ is formed; this is washed with hot water, suspended in water and carbon dioxide and superheated steam passed in for some hours. The violet solution of barium permanganate is filtered from the barium carbonate through asbestos, and crystallised.

Silver permanganate $AgMnO_4$ precipitates from mixed solutions of silver nitrate and potassium permanganate: from a warm solution large crystals deposit on cooling.

Potassium permanganate is a powerful *oxidising agent*. Mixtures with sulphur or charcoal burn like gunpowder, and a mixture of the powder with

powdered oxalic acid crystals inflames spontaneously after a few seconds. The oxidising action is different according as the reaction is carried out in alkaline or in acid solution.

(1) In *alkaline solution* the permanganate is first reduced to green manganate. The solution then deposits brown manganese dioxide and becomes colourless :

$$2MnO_4' + 2OH' = 2MnO_4'' + H_2O + O$$
$$2MnO_4'' + 2H_2O = 2MnO_2 + 4OH' + 2O.$$

Hence two molecules of permanganate in alkaline solution give *three* atoms of available oxygen :

$$2KMnO_4 = K_2O,Mn_2O_7 = K_2O + 2MnO_2 + 3O.$$

Alkaline permanganate oxidises iodides to iodates :

$$2KMnO_4 + H_2O + KI = 2MnO_2 + 2KOH + KIO_3.$$

In *neutral* solution in presence of zinc sulphate or suspended zinc oxide a manganese salt is oxidised to MnO_2 (Volhard, 1879 : a permanganite $ZnMn_2O_5$ may be formed : p. 827) :

$$2KMnO_4 + 3MnSO_4 + 2H_2O = 5MnO_2 + K_2SO_4 + 2H_2SO_4.$$

Hydrogen sulphide precipitates manganous sulphide and sulphur :

$$2KMnO_4 + 4H_2S = 2MnS + S + K_2SO_4 + 4H_2O,$$

but thiosulphate is formed and some dithionate at the beginning of the reaction, the result with 1 p.c. $KMnO_4$ being (Dunnicliff and Nijhawan, *J.C.S.*, 1926, 1) :

$$10KMnO_4 + 22H_2S = 10MnS + 3K_2SO_4 + 2K_2S_2O_3 + 5S + 22H_2O.$$

Thiosulphate is oxidised almost quantitatively to sulphate, a trace of tetrathionate being formed :

$$8KMnO_4 + 3Na_2S_2O_3 + H_2O = 8MnO_2 + 3Na_2SO_4 + 3K_2SO_4 + 2KOH.$$

(2) In *acid solutions* permanganate is reduced to manganous salt and *five* atoms of available oxygen are formed from *two* molecules of permanganate :

$$2MnO_4' + 6H^{\cdot} = 2Mn^{\cdot\cdot} + 3H_2O + 5O$$
$$2KMnO_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 3H_2O + 5O$$
$$2KMnO_4 = K_2O,Mn_2O_7 = K_2O + 2MnO + 5O.$$

Iodine is liberated from potassium iodide :

$$2KMnO_4 + 10KI + 8H_2SO_4 = 6K_2SO_4 + 2MnSO_4 + 5I_2 + 8H_2O,$$

ferrous salts are oxidised to ferric salts :

$$2KMnO_4 + 10FeSO_4 + 8H_2SO_4 = K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O,$$

oxalic acid is oxidised to carbon dioxide :

$$2KMnO_4 + 5C_2H_2O_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O,$$

nitrites are oxidised to nitrates :

$$2KMnO_4 + 5KNO_2 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 3H_2O + 5KNO_3,$$

sulphur dioxide is oxidised to sulphuric acid :

$$2KMnO_4 + 5SO_2 + 2H_2O = K_2SO_4 + 2MnSO_4 + 2H_2SO_4,$$

and hydrogen peroxide forms water and oxygen :

$$2KMnO_4 + 5H_2O_2 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2.$$

Permanganate titrations in presence of hydrochloric acid are unsatisfactory, some hydrochloric acid being oxidised to chlorine. This reaction is *induced* (p. 686) by ferrous ion or oxalic acid, hypochlorous acid being perhaps the first product (Baxter, etc., *Amer. Chem. J.*, 1905, **33**, 500 ; **34**, 109 ; Bassett and Sanderson, *J.C.S.*, 1936, 207). Addition of manganous salt improves the result, since it acts as a catalyst for the main reaction but not for the oxidation of hydrochloric acid.

EXPT. 3.—To a solution of oxalic acid acidified with sulphuric acid and warmed at 60° add $N/10$ $KMnO_4$ solution from a burette. With the first few c.c. the colour is discharged only slowly, but as manganous ion accumulates the colour is quickly discharged.

Cyanogen compounds of manganese.—Potassium cyanide solution gives with manganous salts a yellowish-grey precipitate which may be $Mn(CN)_2$ or $KMn(CN)_3$. This dissolves in excess of cyanide to a yellow solution depositing deep violet-blue tetragonal crystals of **potassium manganocyanide** $K_4Mn^{II}(CN)_6,3H_2O$, which gives a blue precipitate with iron salts (cf. $K_4Fe(CN)_6$). By evaporating a solution of manganocyanide in air oxidation occurs :

$$4Mn(CN)_6'''' + 2H_2O + O_2 = 4Mn(CN)_6''' + 4OH'$$

and a deep red solution of **potassium manganicyanide** $K_3Mn(CN)_6$ is obtained, which forms dark red monoclinic crystals isomorphous with $K_3Fe(CN)_6$. It gives a blue colour with iron salts.

Univalent manganese.—Reduction of alkaline $Na_4Mn(CN)_6$ with aluminium gives a deep yellow liquid which when filtered into sodium cyanide solution saturated with sodium acetate deposits white $Na_5[Mn^I(CN)_6]$ containing *univalent* Mn (Manchot and Gall, 1927–8). The potassium salt $K_5[Mn(CN)_6]$ is formed by electrolytic reduction of $K_4Mn(CN)_6$ (Grube and Brause, 1927).

Rhenium

Masurium and rhenium, first identified by their X-ray spectra (Noddack, Tacke and Berg, 1925), occur in minerals of elements of adjoining groups, *e.g.* in columbite (a tantalum mineral) and in platinum ores, in very small quantities. The chief occurrence of rhenium is in some molybdenites (MoS_2), which may contain as much as 2×10^{-6} g. of Re per g., and it is also extracted from the Mansfeld copper residues, being finally purified by precipitation as nitron perrhenate (see p. 564).

Metallic rhenium, which is white like platinum, is obtained by heating potassium perrhenate or the oxides or sulphides in hydrogen : it oxidises only at high temperatures and is substantially unaffected by acids, except nitric, which converts it into perrhenic acid $HReO_4$. Its electrical resistance is about four times that of tungsten.

Rhenium forms **oxides** Re_2O_7, ReO_3, ReO_2 and Re_2O_3. The most characteristic is the stable **heptoxide**, a pale yellow crystalline solid formed by burning rhenium

in oxygen. It begins to sublime at 220°, m.p. 301·5°, b.p. 363°. By subliming Re_2O_7 over heated rhenium, a purplish-red solid **trioxide** ReO_3 decomposing at 300° is obtained. A green **barium rhenate** $BaReO_4$ corresponds with an unknown rhenic acid H_2ReO_4. The black non-volatile **dioxide** is formed by reducing Re_2O_7 with hydrogen; brown alkali **perrhenites** (or rhenites) Na_2ReO_3 and K_2ReO_3 are formed on fusing ReO_2 with alkali hydroxides. Hydrated rhenium **sesquioxide** Re_2O_3 is obtained by the action of alkali on the trichloride $ReCl_3$: it is easily oxidised and liberates hydrogen from water.

Rhenium heptoxide is remarkably soluble in water, forming **perrhenic acid** (up to 65 p.c. by weight of $HReO_4$), which is reduced only with difficulty. The solution is strongly acid, attacking most metals and dissolving the carbonates easily. The perrhenates are very characteristic and stable. The ion is colourless. $KReO_4$ (which can be melted without decomposition) is much less soluble than $NaReO_4$ (compare the permanganates). On reduction, perrhenate solutions exhibit a series of colour changes corresponding with lower valency states.

The **hexafluoride** ReF_6, m.p. 25·6°, b.p. 47·6°, is formed from the elements; it is easily reduced by hydrogen to the **tetrafluoride** ReF_4, m.p. 124·5°. **Oxyfluorides** are $ReOF_4$, m.p, 39·7°, b.p. 62·7°, and ReO_2F_2, m.p. 156°. The black crystalline **pentachloride** $ReCl_5$ is formed from the elements at 250° and is volatile in chlorine. It dissolves in a little water to a blue solution but is hydrolysed by excess to black hydrated ReO_2. On heating in nitrogen it forms the **trichloride** $ReCl_3$. There is also a **tribromide** $ReBr_3$. The yellowish-green complex salts $M_2^I[Re^{IV}Cl_6]$ are formed, with chlorine, by heating $ReCl_5$ with alkali chlorides. By the interaction of $ReCl_5$ and Re_2O_7 the **oxychlorides** $ReOCl_4$ (brown, m.p. 28°) and ReO_3Cl (yellow or colourless, m.p. 4·5°, b.p. 131°) are formed.

Rhenium forms **sulphides** and **selenides**, Re_2S_7, ReS_2, and Re_2Se_7, $ReSe_2$. The quantitative precipitation of Re_2S_7 by H_2S from a hot solution in concentrated HCl is a method of determination. **Thioperrhenic acid** $HReS_4$ exists in solution and as the solid thallous salt $TlReS_4$.

CHAPTER XXX

THE EIGHTH GROUP: IRON, COBALT AND NICKEL

THE eighth group comprises the *inert gases* with completed 8-electron outer shells, and three **triads** of Mendeléeff's *transitional elements*:

Group VIII (*a*)

	At. No.	Electron configuration	Density	At. Vol.	M. Pt.	B.Pt.
Iron	26	2·8·14·2	7·86	7·1	1539°	2450°
Cobalt	27	2·8·15·2	8·8	6·7	1478°	2900°
Nickel	28	2·8·16·2	8·8	6·7	1452°	2900°
Ruthenium	44	2·8·18·15·1	12·26	9·6	2450°	>2700°
Rhodium	45	2·8·18·16·1	12·4	9·8	1970°	>2500°
Palladium	46	2·8·18·18·0	11·9	8·96	1553°	2200°
Osmium	76	2·8·18·32·14·2	22·48	8·5	2750°	>5300°
Iridium	77	2·8·18·32·15·2	22·42	8·6	2440°	>4800°
Platinum	78	2·8·18·32·17·1	21·4	9·1	1755°	4300°

The atomic weights in these triads are more nearly alike than in other parts of the periodic table. These transitional elements are really central triads in periods of transitional elements in the wider sense (p. 261), as Mendeléeff already pointed out:

Cr	Mn	Fe	Co	Ni	Cu	Zn
Mo	—	Ru	Rh	Pd	Ag	Cd
W	Re	Os	Ir	Pt	Au	Hg

there being a gradation of properties along each period. The resemblance between Fe, Co, Ni and the platinum metals from Ru to Pt is not very close, and is seen mainly in the marked tendency to form complex compounds, which nickel shows in a much smaller degree:

$$K_4[Fe(CN)_6] \qquad K_3[Co(NO_2)_6] \qquad K_2[PtCl_6] \qquad Na_2[OsCl_6],2H_2O$$

There are some resemblances in the vertical groups Fe, Ru, Os, Co, Rh, Ir and Ni, Pd, Pt, but on the whole this is much less important than in the other groups of the periodic system.

The platinum metals in their generally "noble" character, tendency to complex formation, and high densities show close analogies with gold. They are all paramagnetic, palladium in the highest degree; Fe, Co and Ni are ferromagnetic. All the metals have high m.ps.

As transitional elements the metals of Group VIII *a* show a large number of valencies, the valency suddenly dropping to zero with the inert gases of Group VIII *b*; the valencies are:

Fe	1, **2**, **3**, 6	Ru	1, 2, **3**, 4, 5, 6, 7, 8	Os	2, 3, **4**, **6**, 7 (?), **8**
Co	1 **2**, **3**, 4	Rh	1, 2, **3**, 4, 6	Ir	1, 2, **3**, 4, 5, **6**
Ni	1, **2**, 3, 4	Pd	1 (?), **2**, 3, **4**	Pt	1, **2**, 3, **4**, 6

the predominating valencies being in heavy type. The appearance of the maximum valency of 8 (the typical valency of the group) in the case of Ru and Os is noteworthy, as is the tervalency of ruthenium and rhodium and the bivalency of palladium in the common compounds.

Although the platinum metals are generally "noble" and not easily attacked by acids, ruthenium and osmium oxidise easily on heating in air or especially oxygen (in which they burn) forming the volatile oxides RuO_4 and OsO_4, and palladium becomes covered with a blue film of oxide on heating in air. All these elements form lower basic oxides.

Iron, cobalt and nickel oxidise on heating in air and decompose steam at a high temperature, nickel much less readily than iron and cobalt. The lower oxides $M^{II}O$ are strong bases, the oxides $M_2^{III}O_3$ are much less basic and are amphoteric; the corresponding salts are stable only in the case of iron, Fe_2O_3 forming *ferrites* such as $Na_2Fe_2O_4$. The oxides M_3O_4 are of the type $M^{II}O,M^{III}{}_2O_3$ or $M^{II}(M^{III}O_2)_2$, *i.e.* spinels (p. 422). Iron forms *ferrates* derived from an unknown acidic trioxide $Fe^{VI}O_3$ which resemble chromates and manganates: K_2FeO_4, K_2CrO_4, K_2MnO_4. The metals iron, chromium and manganese are similar in physical properties.

The order of the elements Fe, Co and Ni in the first transition period is in the reverse of that of the atomic weights in the case of cobalt and nickel (p. 176), but agrees with many of the chemical properties. Cobalt closely resembles iron and nickel resembles copper, which follows it in the long period (p. 182). The ease of reduction of the oxides increases in the order Fe, Co, Ni and Cu, and hence the action of the heated metals in decomposing steam follows the reverse order, nickel and copper reacting only at very high temperatures. In the tendency to form stable compounds in which it is bivalent, nickel also resembles copper and palladium (which is vertically below it in the Periodic Table), whilst iron, cobalt, ruthenium and rhodium show a tendency to form compounds in which they are tervalent (cobalt in the very stable cobaltammines, etc., but not in the simple salts). The tendency to form complex compounds in which they are tervalent is strong with iron and cobalt, but lacking with nickel.

Iron, cobalt, nickel, ruthenium, iridium and osmium form covalent *carbonyls* with carbon monoxide (p. 875). These compounds bear no relation to the normal valencies of the metals and are chiefly but not always formed by donation of electrons from the carbon monoxide molecules.

Iron

Metallic iron was known in Predynastic Egypt (before 3400 B.C.), but was very scarce and was used only for beads (Petrie). It was probably meteoric, as it contains nickel. Iron came into general use in Egypt about 1500 B.C., and seems to have spread from the Hittites of Asia Minor. In 600 B.C. it was much

used in Assyria. The Etruscans worked the mines of Elba, later taken over by the Romans, who also worked the mines of Spain and Noricum. Iron was worked at an early date in India and China.

Iron rarely occurs native. Large masses occur in Disko Island, West Greenland, and grains in basalt at Giant's Causeway and elsewhere. Meteorites sometimes consist of metallic iron with 3–30 p.c. of nickel and some occluded hydrogen, and iron must be present in the solar system. The inner core of the earth is supposed to be largely metallic iron.

Meteorites may consist partly or principally of silicates (*e.g.* olivine) and glassy minerals (moldavite), although grains of metallic iron usually occur even in stony varieties. On account of the nickel content, meteoric iron does not easily rust. Other constituents of meteorites are cobalt, graphite (sometimes small diamonds), ferrous sulphide, and *schreibersite* $(Fe,Ni,Co)_3P$ and *cohenite* $(Fe,Co,Ni)_3C$, which are not known as terrestrial minerals. Meteoric dust consisting chiefly of iron is constantly falling on the earth from space.

After aluminium, iron is the most plentiful terrestrial metal (p. 3). Iron compounds occur in the soil, many minerals and rocks, green plants, and in haemoglobin (0·336 p.c. Fe), the red colouring matter of blood.

Iron ores are plentiful but few in number. The value of an ore depends mainly on its freedom from impurities (S, P, As, etc.) which are detrimental to the resulting metal. The most important ores are the *oxides* Fe_3O_4 and Fe_2O_3, *hydrated ferric oxides* Fe_2O_3,xH_2O, and *ferrous carbonate* $FeCO_3$.

The *black oxide* Fe_3O_4 occurs as *magnetite*, so called because certain varieties (lodestone) are permanently magnetic. It is not found to any extent in Great Britain, but occurs in Lapland, Sweden, Siberia (Urals), Germany, India (Madras) and North America (Lake Superior). When pure it contains 72·4 p.c. of iron and is the richest ore. *Ferric oxide* Fe_2O_3 occurs as *haematite*, sometimes crystalline and red (or if black giving a red streak on unglazed porcelain), also in earthy, granular, and nodular forms, and is found in England in the Furness district in Lancashire, and near Whitehaven, in Belgium, Westphalia, Sweden, the Island of Elba, south of Lake Superior and near St. Louis (Missouri). *Hydrated ferric oxide* occurs as *limonite* in kidney-shaped masses in Great Britain in South Wales and the Forest of Dean, in France, Germany, Bilbao in Spain, and Canada. The so-called *bog iron ores*, found in large amounts in Ireland, Sweden, and North Germany, are hydrated ferric oxides. The only remaining important ore is *ferrous carbonate* $FeCO_3$, occurring either alone as *siderite*, *chalybite*, or *spathic iron ore*, or as the most important British ores *clay-ironstone* (mixed with clay) and *blackband ironstone* (mixed with clay and coal). Pyrites cinders, chiefly ferric oxide, from the roasted pyrites used in sulphuric acid manufacture, are desulphurised by roasting and are smelted for iron.

The metallurgy of iron.—Three varieties of commercial iron—cast iron, wrought iron, and steel—are made from ores in the following order:

Ore→*Cast Iron* (*Pig-iron*) → *Wrought iron*→*Crucible Steel*
Ore→*Cast Iron* (*Pig-iron*) → *Bessemer*, or *Open-Hearth*, *Steel.*

The extraction of iron from the ores involves a number of processes (Turner, *The Metallurgy of Iron*, 4th edit., 1915; Stoughton, *The Metallurgy of Iron and Steel*, 3rd edit., New York, 1923; Harbord and Hall, *The Metallurgy of Steel*, 7th edit., 2 vols., 1923).

(1) *Preliminary roasting or calcination* is used with carbonate or hydrated ferric oxide ores to drive off moisture and carbon dioxide and convert ferrous iron into ferric oxide.

It is carried out by stacking the ore with a little coal in heaps, or in shallow kilns or in shaft-furnaces, and regulating the temperature and air supply so that most of the moisture, carbon dioxide, sulphur and arsenic are expelled, and ferrous converted to ferric oxide to avoid the formation of ferrous silicate in slag during smelting. The ore is also made more porous. Powdery ore is agglomerated by sintering or briquetting.

(2) *Smelting*, by reducing the ore by carbon in the blast furnace. The *blast furnace* (introduced in a simple form about 1450) consists (Fig. 335) of an

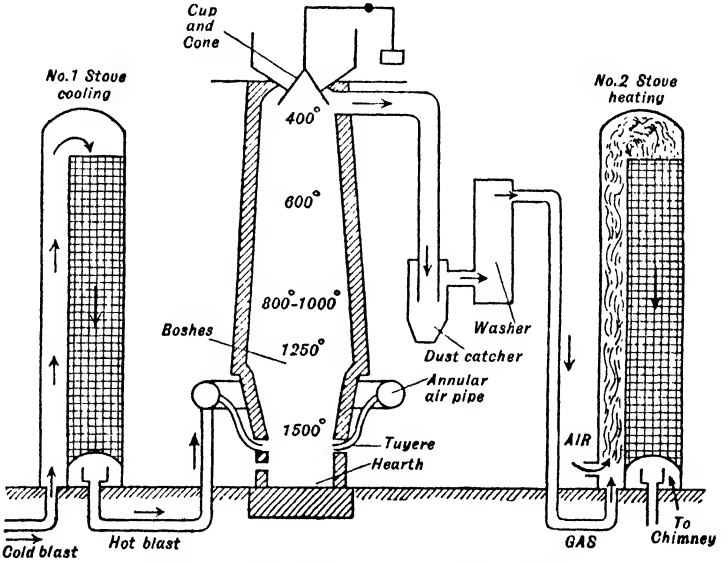


FIG. 335.—Blast furnace and Cowper stoves.

outer shell of steel plates lined with refractory bricks. It is 50–100 ft. high, the greatest width being about 24 ft. at the "boshes." The mouth is closed with a *cup-and-cone* through which the charge of ore, limestone and fuel is fed intermittently by lowering the cone. In large furnaces a double cup-and-cone is used, one being closed when the other is opened, which prevents escape of gas.

The gas (chiefly carbon monoxide and nitrogen) passes through a pipe to a *dust-catcher* and a *washer*, and is then used in the Cowper stoves (see below) for heating the air blast.

The furnace below the boshes narrows to a *hearth* at the base, pierced with holes for the water-jacketed iron blowing-pipes or *tuyeres*, through which air is forced from an annular pipe by powerful blowing engines. The hearth is also pierced below the tuyeres with a *tapping hole*, stopped with clay, from which molten iron is periodically tapped into sand moulds on the ground, and a *slag notch* at a rather higher level, from which the molten slag runs continuously from above the molten iron.

About 3–5 tons of air are passed per ton of iron made, the power for the blowing engines being supplied by coke-oven gas. Coal is usually first coked in ovens for the furnace charge, but in Scotland raw coal is used and charcoal is used in Sweden.

The composition of the charge is 1 ton of hard oven-coke, 8–12 cwt. of limestone to form the slag (calcium and aluminium silicates) and so much ore (say 2½ tons) as produces 1 ton of iron. The process is continuous and each furnace may produce 300 tons of iron per 24 hours. A higher production can be got with a higher blast pressure.

The air blast is preheated to 700°–800° by passing through *Cowper stoves*, which are tall iron cylinders lined with firebricks and packed with chequer brickwork with a circular flue on one side. Part of the hot furnace gas with enough air to burn it passes through one set of stoves until the bricks are red-hot, the products of combustion escaping through a chimney. The gas is then turned through a second set of stoves and the air blast to the tuyeres sent through the first until the temperature of the brickwork has fallen. Two sets of stoves are thus used alternately as heat-regenerators, and this economises fuel and the furnace works at a higher temperature.

The normal composition of *blast furnace gas* by vol. is: N_2 60, CO 24, CO_2 12, H_2 and CH_4 4. It is mostly used for heating the stoves, but in some works is used partly in steam boilers for the blowing engines or as fuel for gas engines. In some cases a *dry blast* is used, the air being first cooled by refrigeration or passed over silica gel to remove moisture, when loss of heat due to the endothermic reaction $C + H_2O = CO + H_2$ in the blast furnace is prevented.

The *chemical reactions in the blast furnace* may be summarised as follows:

(i) The oxygen of the blast combines with carbon at a very high temperature in the hearth to form carbon monoxide: $2C + O_2 = 2CO$. The temperature of the charge passing down the furnace increases continually from the mouth to the hearth.

(ii) Above the boshes, at a dull red heat, ferric oxide is reduced by carbon monoxide to spongy iron: $Fe_2O_3 + 3CO \rightleftharpoons 2Fe + 3CO_2$. The reaction is reversible and the escaping gas contains CO and CO_2 in the ratio 1 : 0·5. Some oxide may be directly reduced by carbon at the highest temperature in the hearth.

(iii) In the upper zone the limestone is decomposed: $CaCO_3 \rightleftharpoons CaO + CO_2$, and some carbon dioxide is reduced to monoxide: $CO_2 + C \rightleftharpoons 2CO$. The spongy iron absorbs sulphur from the fuel.

(iv) Near the centre of the furnace, at a bright red heat, finely divided carbon is deposited from the reaction: $2CO \rightleftharpoons C + CO_2$. This and the carbon of the charge complete the reduction: $Fe_2O_3 + 3C = 2Fe + 3CO$.

(v) In the central zone phosphorus is formed by reduction of phosphates in the ore in presence of iron and silica: $P_2O_5 + 5Fe + 5SiO_2 = 5FeSiO_3 + 2P$, and is absorbed by the iron. At a higher temperature some silicon is formed by reduction of silicates by iron and carbon, and alloys with the iron. The silica and lime (and any alumina in the ore) form a fusible slag which usually contains some calcium sulphide CaS. Manganese is also formed by reduction of manganese compounds in the ore, and alloys with the iron.

(vi) At a white heat in the lowest part of the furnace the spongy iron containing carbon, silicon and manganese, and the impurities sulphur and phosphorus, fuses and is tapped off to form pig-iron or send fluid to the steel furnaces.

Cast iron or *pig-iron* contains 2·2–4·5 p.c. of carbon, together with silicon, manganese, sulphur and phosphorus. When the cooling is rapid, the silicon content small and the manganese high, *white pig-iron* is formed, in which the carbon is in the form of iron carbide or *cementite* Fe_3C. It is brittle, coarsely crystalline, and nearly completely soluble in dilute hydrochloric acid, evolving hydrogen and hydrocarbons. If the molten iron containing at least 2·5 p.c. of silicon is *slowly* cooled, most of the carbon separates in fine flakes of *graphite*, the iron becoming softer and of finer texture. This *grey pig-iron* on solution in dilute hydrochloric acid evolves chiefly hydrogen and leaves a black residue of graphite. An intermediate variety is *mottled pig-iron*. The solubility of carbon in pure iron is 4·25 p.c., but more is dissolved in presence of manganese.

Malleable or wrought iron is nearly pure iron, containing only 0·12–0·25 p.c. of carbon; it melts at a higher temperature (1400°–1500°) than cast iron and contains less than 0·5 p.c. of total carbon, silicon, sulphur and phosphorus.

Malleable iron can be made from cast iron by the *puddling process* (Cort, 1784). The cast iron is fused in a reverberatory furnace with material containing iron oxide, which oxidises the carbon: $Fe_2O_3 + 3C = 2Fe + 3CO$, the carbon monoxide bubbling through the molten iron. Sulphur, phosphorus and silicon first oxidise and pass into the slag. When the metal becomes pasty it is formed into lumps or "blooms" which are beaten under a steam hammer to squeeze out the slag. The iron welds together to a coherent mass below 1000°. Mechanical puddling furnaces are used in America.

Malleable or wrought iron is tough and fibrous; its softness is not much altered by heating to redness and quenching in water, whereas steel becomes very hard. Wrought iron is now mostly replaced by mild (low carbon) steel.

Wrought iron containing phosphorus is brittle at the ordinary temperature and is said to be *cold-short*; sulphur, probably as FeS, makes the iron brittle at a red heat, when it is called *red-short*. The effect of sulphur is reduced if manganese is present, as this forms MnS, and that of phosphorus by copper or chromium or both.

If cast iron is cast in a metal mould to cause rapid cooling the cementite, Fe_3C, may be decomposed by heating the casting, embedded in haematite, for

several days. The combined carbon in the surface is oxidised and that from the interior diffuses out to replace it. Finally the carbon content is reduced to that of steel, and a *malleable casting* is produced. Sometimes the cementite in the interior is caused to decompose with separation of fine graphite and the iron becomes soft. The result is a " black-heart casting," white outside with a black core.

Steel is iron which has been fused in the process of manufacture and has a carbon content from 0·15 p.c. (very soft or " mild " steel) to 1·5 p.c. or more (very hard steel). It may also contain special constituents, such as manganese and other metals. Steel is made :

(i) from pure wrought iron by adding carbon (*cementation process*) ;
(ii) from cast iron by removing part of the carbon, and refining (*Bessemer process*) ;
(iii) by melting suitable amounts of cast iron and wrought iron or mild steel scrap under such conditions that refining occurs and the carbon content of the resulting metal is suitably adjusted (*Siemens-Martin, or open-hearth, process*) ;
(iv) directly from pure ore and carbon in the electric furnace.

Most modern steel is made from cast iron by removing part of the carbon and refining by the Bessemer or the Open-Hearth process.

Steel also contains small amounts of other elements besides carbon, but the impurities in cast iron (silicon, manganese, sulphur and phosphorus) are mostly removed. Analyses of cast iron and the steel made from it illustrate this :

	Fe	C	Si	P	Mn	S
Cast iron -	93·2	1·0	1·4	2·5	1·8	0·1
Steel - -	99·3	0·18	0·004	0·02	0·44	0·042

The cementation process.—When wrought iron is made from pure oxide ores by reduction with charcoal it is converted into high-grade steel by the cementation process.

Bars of wrought iron surrounded with charcoal powder are heated in fireclay boxes in a furnace for one or two weeks. The iron absorbs carbon, the carbonisation spreading slowly through the mass and converting the iron into steel. The surface of the bars is covered with blisters, and the " blister steel " is fused in plumbago crucibles to form *cast steel* or *crucible steel* (Huntsman, of Sheffield, 1740).

It has been stated that pure carbon, free from gases, does not penetrate iron except under high pressure, so that carbon monoxide may be the active agent, although hydrocarbon gases, cyanogen and cyanides also cause cementation.

Wrought iron is *case-hardened* by heating in contact with carbon or potassium ferrocyanide, etc., when a surface-layer of steel is formed. *Armour plate* is made by case-hardening a sheet of soft steel on one side and spraying with cold water when red-hot. Nickel-chromium steels form very tough armour plate and after heat treatment are used for projectiles. A very hard surface, used for cylinder bores, etc., is formed by *nitriding, i.e.* heating steel containing about 1 p.c. of aluminium at 450°–500° in an atmosphere of ammonia. Iron nitrides

(Fe_2N, etc.) are formed in the interstices of the iron crystals and prevent gliding of the latter under stress.

The Bessemer process.—In this (Henry Bessemer, 1855) molten pig-iron is run from the blast furnace into a *converter* (Fig. 336) consisting of a large pear-shaped iron vessel holding 10 tons of metal, lined with refractory bricks, and supported on trunnions. In the " acid " Bessemer process the converter is lined with silica bricks, in the " basic " process with a mixture of lime and magnesia.

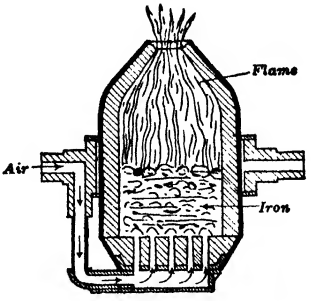


FIG. 336.—Bessemer converter (section).

Air is led by a pipe to the hollow perforated base of the converter, through which it is forced in bubbles through the molten metal. The charging is carried out with the converter horizontal and blowing is begun. The converter is then swung into a vertical position and blowing continued. Silicon and manganese first oxidise, producing most of the heat, and pass into the slag, and then the carbon oxidises to carbon monoxide, which is now freely evolved from the molten iron, and burns at the mouth of the converter with an orange-yellow flame, edged with blue and shot through by showers of brilliant sparks. After 6–8 mins. the flame sinks, indicating that the carbon has been completely removed. Owing to the high temperature the pure iron is still fluid.

The converter is again tilted, the blast is stopped, and the requisite amount of *spiegeleisen* (" mirror-iron "), an iron-carbon-manganese alloy, is added to form the steel. This method of carburising the metal, which is an essential part of the Bessemer process, was introduced by Mushet in 1856. The molten steel is poured, by tilting the converter, into ladles supported by travelling cranes, from which it is run into moulds. A little aluminium, or silicon-iron alloy (*silicon spiegel*), or titanium-iron alloy, may be added to the molten steel to prevent blow-holes in the castings, due to bubbles of gas, which combine or react with the aluminium, silicon or titanium.

According to the percentage of carbon added various kinds of steel are produced: *tool steel* (0·9–1·5 p.c. C), *structural steel* (0·2–0·6 p.c. C), and *mild steel* (0·2 p.c. C or less).

Ores of iron containing phosphate give cold-short iron (p. 839), which may be worked to give good steel by the *basic process* of Thomas and Gilchrist (1879), in which the converter has a " basic " lining of magnesia and lime, made by calcining dolomite. In this process the sulphur is also removed. Limestone is first charged into the converter with coke and the blast is turned on. Molten pig-iron is run in, the converter tilted and the blowing continued. Silicon and manganese first burn out, then carbon and some of the phosphorus, producing most of the heat, oxidise simultaneously. When the carbon is burnt out the flame at the mouth of the converter sinks, but the blast is prolonged to burn out the remaining phosphorus. The P_2O_5 combines with the lime of the

limestone added (*not* mainly that of the converter lining) to form *basic slag*, $Ca_4P_2O_9$, a valuable fertiliser. Before the spiegeleisen is added the basic slag must be removed, otherwise the phosphorus would pass back into the iron. The slag may be removed from the converter, or the spiegeleisen added to the steel in the ladle. It is possible by the basic process to treat pig-iron containing as much as 3 p.c. of phosphorus.

The open-hearth process was suggested by Réaumer in 1722 but was first worked on the technical scale by the brothers Martin in 1864 in France, who made use of the regenerative heating process of Sir William Siemens. It is carried out on a large flat hearth enclosed in a furnace (Fig. 337), heated by producer gas. The gas and air are supplied through separate chequer brickwork regenerators used in pairs and traversed alternately by air and producer gas, and by hot burnt gas from the furnace, as in Cowper stoves (p. 838). The

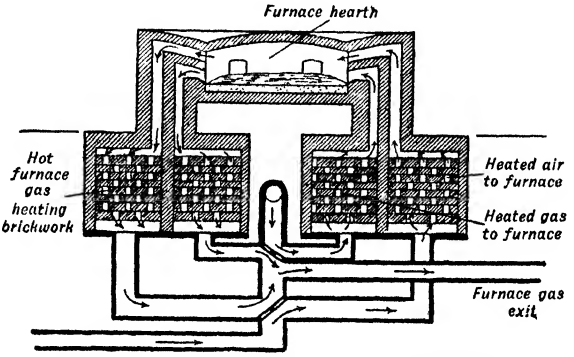


FIG. 337.—Open-hearth steel furnace (section).

hearth is lined with silica in the acid process and calcined magnesite or dolomite in the basic process. The charge consists of pig-iron (part of which may be run in liquid from the blast furnace ladle) and steel scrap, with lime or limestone in the basic process. By the blending of pig-iron and steel scrap and the refining process molten steel is formed. Sodium carbonate may be added for desulphurising ; the phosphorus is removed as described above. In another process pig-iron and iron ore (which oxidises part of the carbon in the pig-iron) are used. The furnace may be made to tilt and discharge part of its content into a ladle.

The open-hearth process lasts 8–10 hours and is slower and easier to work than the Bessemer process. It is largely used in Great Britain, but it calls for a large amount of steel scrap, so that the Bessemer process is much used on the Continent and in America.

A very pure iron (*Armco iron*) is made by a modification of the open-hearth process using a very basic slag and a high temperature, followed by addition of aluminium. It contains less than 0·1 p.c. of total impurity and is almost rustless.

Electric furnaces are used in making special high-quality *alloy steels* which have numerous valuable properties. Constituents of alloy steels include

chromium, cobalt, manganese, molybdenum, nickel, silicon, titanium, tungsten and vanadium, and often more than one of these. The electric furnace is generally used to refine steel scrap or steel from Bessemer or open-hearth furnaces, the special constituents being then added.

Silicon steel (about 3·5 p.c. Si and very little C), with the silicon in solid solution, is used for transformers, silico-manganese steels for springs, and silico-chrome steels for exhaust valves. *Manganese steel* is air-hardened, *i.e.* becomes hard after cooling in air. *Tungsten steel* remains hard at a red heat and is used for cutting-tools. Some special steels are described in the sections on chromium, cobalt, etc.

The electric steel furnace is usually on the arc principle, with large vertical carbon electrodes between which and the charge electric arcs are struck. Sometimes the arc is between the electrode and a conducting base.

The properties of steel.—The properties of steel depend largely on the heat treatment and the carbon content: low-carbon steels are soft like wrought iron and are known as *mild steel*; with more carbon the ductility falls, whilst the tensile strength increases up to the limiting percentage of 1·5 of carbon. Cast iron has a tensile strength of 10 tons per sq. in., wrought iron of 25 tons, and steel of 30–100 tons. Wrought iron and steel are malleable and may be welded. The melting point of steel is lower than that of wrought iron. The properties of steel depend on the *heat treatment* of the metal. If steel is heated to redness and quenched in cold water it becomes as hard and brittle as glass. If it is now heated to various temperatures the resulting metal possesses properties depending on the temperature. This process is called *tempering*, and the temperature is judged by the colour of the thin film of oxide produced on a bright surface of the metal:

230°: light-straw colour: used for razor blades.
255°: brownish-yellow: used for penknives and axes.
277°: purple: used for cutlery.
288°: bright blue: used for watch-springs and swords.
290°–316°: dark blue: used for chisels and large saws.

Allotropic forms of iron.—Three allotropic forms of iron recognised are: (1) α-iron (or *α-ferrite*), stable below 912°, soft, magnetic, capable of dissolving but little carbon, body-centred cubic lattice: this is the chief constituent of pure wrought iron. (2) **γ-iron** (or *γ-ferrite*), stable from 912° to 1400°, non-magnetic, dissolving carbon to form a solid solution, face-centred cubic lattice. (3) **δ-iron** stable above 1400°, does not dissolve carbon, body-centred cubic lattice, may be the same as α-iron. The phase-changes are thus:

$$\alpha\text{-Fe} \overset{912^\circ}{\rightleftharpoons} \gamma\text{-Fe} \overset{1400^\circ}{\rightleftharpoons} \delta\text{-Fe}.$$

Iron loses its ferro-magnetism at about 760°, but this is not due to an allotropic change to a β-iron, as was once thought.

The iron-carbon system.—When steel containing carbon and also nickel or manganese is heated and quenched it forms a homogeneous non-magnetic solid

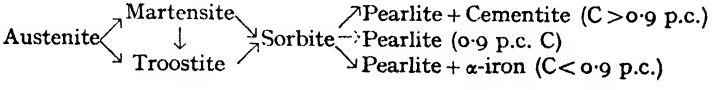
solution of carbon in γ-iron called **austenite**, with a structure of relatively soft large crystals. Nickel or manganese retards the conversion of γ- into α-iron which would otherwise occur below 912° and form a heterogeneous mixture of soft α-iron and hard grains of iron carbide or **cementite**, Fe_3C. Cementite forms rhombic crystals, insoluble in dilute acids, so that it can be isolated from steel by the action of dilute sulphuric acid and potassium dichromate. A carbon steel not stabilised by manganese or nickel forms on heating and quenching a very hard steel with a needle-like structure and tetragonal lattice, called **martensite**, a primary metastable stage in the breaking down of austenite into α-iron and cementite. The formation of martensite is co-extensive with hardness in the steel. Less rapid cooling of iron containing only a little carbon forms a mixture of crystals of α-iron and **pearlite**, a finely laminated eutectoid structure (see below) of alternate layers of α-iron and cementite, with an average carbon content of 0·9 p.c. and formed at 695°.

Hard martensitic steel is formed only on cooling faster than a critical hardening speed, which is very high for carbon steels but much smaller for alloy steels, which can sometimes be hardened even by air-cooling. If the steel is cooled rapidly but below the critical hardening speed it forms **troostite**, another transitional substance from the breakdown of austenite into pearlite but formed at a much higher temperature than martensite. It is formed on cooling heated carbon steels in oil and is about half as hard as martensite, from which it can also be formed.

Another transitional stage in the less rapid cooling of a steel containing manganese is **sorbite**, which has a very finely laminated pearlite structure with great tenacity and ductility; it is best produced by first hardening and then tempering at about 650°.

The structure of a hardened and fully tempered steel consists of small spherical particles of the very hard cementite Fe_3C uniformly distributed in a soft ferrite (iron) matrix; it is often called *true sorbite* and has great tenacity and ductility.

According to the carbon content, pearlite or mixtures of pearlite with cementite or with α-iron (ferrite) may be formed. When very slowly cooled the cementite breaks down into soft α-iron and scales of graphite (Carpenter and Robertson, *Metals*, 1939, **2**, 880; Simons and Gregory, *The Structure of Steel*, 1938):



In Fig. 338, A is the m.p. 1539° of pure iron (δ-iron). This is lowered by carbon along the liquidus curve AB, a solid solution of carbon in δ-iron separating. At B a transition of Roozeboom's Type IV (p. 67) occurs, and along BC a solid solution of carbon in γ-iron, *austenite*, separates. The transition point of δ-iron into γ-iron is shown on the vertical axis at 1400°. DE is the solidus curve for austenite, and represents the lowering of m.p. due to the solution of carbon in solid iron. C is a eutectic point (1125°) at which the mass solidifies to a mixture of austenite and cementite (Fe_3C). The curves show that if the molten iron contains less than 1·8 p.c. of carbon it may solidify entirely to austenite, whilst liquids containing more than 4·3 p.c. of carbon deposit cementite. CH is the solubility curve of cementite.

On further cooling the solid, the solubility of carbon in γ-iron decreases, and cementite is deposited from the solid mass. The percentage of carbon in solution in the austenite decreases along *EF*, the point *F* corresponding with 0·87 p.c. of carbon. At 912° the γ-iron changes to α-iron, which does not form a solid solution with carbon. The carbon dissolved in γ-iron depresses the transition point of γ-iron into α-iron along *GF*, *F* being a *eutectoid point* where the remaining austenite is converted into a mechanical mixture (*eutectoid*) of α-iron and cementite which is called *pearlite*. Below 700° no further phase-changes occur.

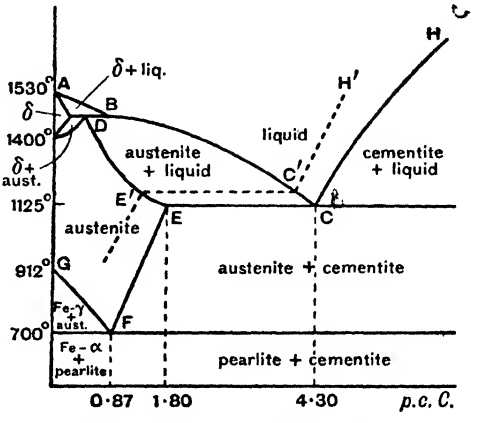


FIG. 338.—The iron-carbon system.

Alloys with less than 0·87 p.c. of carbon are called *hypoeutectoid*, those with between 0·87 and 1·8 p.c. *hypereutectoid*, alloys. The alloy at *C* with 4·3 p.c. of carbon is the *eutectic* alloy, those with 1·8 to 4·3 p.c. are *hypoeutectic*, and those with 4·3 to 5 p.c. of carbon are *hypereutectic*, alloys.

When graphite separates instead of cementite, as sometimes occurs on very slow cooling, the points *E* and *C* are raised to *E'* and *C'*, and *C'H'* is the solubility curve of graphite. It intersects *BC* at 1137°. The magnetic transformation occurs at about 700°, but does not represent a phase-change. The thermal change taking place in it is the cause of *recalescence*, the sudden reheating of a mass of red-hot iron on slow cooling.

The various changes evolve heat and can be followed by observing the temperature of the cooling metal by a pyrometer. The separation of the various constituents may be observed by quenching, polishing, etching the surface with various reagents, and examining microscopically.

Pure iron.—The soft iron wire used for binding flowers contains 99·7 p.c. of iron. *Armco iron* (p. 842) is 99·9 p.c. Fe. Very pure iron (Roeser and Wensel, *J. Res. Bur. Stand.*, 1941, **26**, 273) is difficult to make. It may be obtained by reducing pure ferric oxide (made by heating recrystallised ferric nitrate) in hydrogen at 1000°, or by electrolysis of a solution of ferrous sulphate or chloride, or ferrous ammonium sulphate, and melting in a vacuum. Pure iron is soft and almost white. It is permeated by hydrogen at about 350°, the permeability increasing rapidly up to a red heat, and it burns brilliantly in oxygen when heated.

Carbonyl iron in fine powder is made by injecting iron carbonyl $Fe(CO)_5$ vapour into a space heated by radiant heat at 200°–250°. It is quite pure except for traces of carbon and oxygen. By fusing in an induction furnace with

the requisite amount of pure ferric oxide (obtained from iron carbonyl) the carbon may be reduced below 0·0007 p.c. and the oxygen below 0·01 p.c.

Electrolytic iron is brittle because of its fine crystalline structure and can be powdered; it contains occluded hydrogen which is removed by heating in vacuum. The powder (or grains of carbonyl iron) may be pressed with an adhesive into *Pupin coils*, with very low hysteresis losses and used in some electrical devices.

Reduced iron is a black or grey powder obtained by heating ferric oxide in hydrogen. When prepared from pure oxide (from the nitrate, carbonate or oxalate of iron) at fairly low temperature (about 435°) it is pyrophoric, owing to its fine state of division.

Iron readily occludes hydrogen, nitrogen and carbon monoxide, the solubility increasing with rise in temperature and showing a marked alteration about 936°. The excess of gas is liberated on cooling the molten metal, and that retained by the solid by heating in vacuum. During the passage of hydrogen through heated iron or steel, the carbon, sulphur and phosphorus are removed as gaseous hydrides and the metal becomes soft.

Iron does not easily amalgamate, but *iron amalgam* is obtained by rubbing iron powder with mercuric chloride and water, by electrolysing saturated ferrous sulphate solution with a mercury cathode, or by the action of sodium amalgam on ferrous chloride solution: 1 p.c. sodium amalgam gives 1·29 p.c. iron amalgam.

The rusting of iron.—Ordinary iron exposed to ordinary moist air is quickly corroded to a reddish-brown rust, consisting of hydrated ferric oxide, mainly *lepidocrocite* Fe_2O_3,H_2O or FeO(OH) (p. 856), with a little ferrous hydroxide and carbonate in fresh rust (Dunstan, etc., *J.C.S.*, 1905, **87**, 1548; Gates, *T. Faraday Soc.*, 1933, **39**, 817). The conditions under which rusting takes place have been investigated by several experimenters, with somewhat divergent results (J. N. Friend, *The Corrosion of Iron and Steel*, 1911; Hudson, *The Corrosion of Iron and Steel*, 1940). The homogeneity and purity of the metal affect the results. The presence of water is essential and according to some experimenters carbon dioxide or acidity is also necessary.

Crace Calvert (1876) and Crum Brown (1888) suggested the following reactions:

$$Fe + H_2O + CO_2 = FeCO_3 + H_2$$
$$4FeCO_3 + 6H_2O + O_2 = 4Fe(OH)_3 + 4CO_2.$$

According to G. T. Moody (*J.C.S.*, 1906, **89**, 720), pure iron does not rust in presence of water and air if every trace of carbon dioxide is excluded. The iron first passes into solution, when carbon dioxide is present, as ferrous bicarbonate $Fe(HCO_3)_2$, which is then oxidised by dissolved oxygen with precipitation of ferric hydroxide. Alkali added to the water retards rusting (Rinman, 1782). Lambert (*J.C.S.*, 1910, **97**, 2426; 1912, **101**, 2056; 1915, **107**, 210) found that pure iron remained bright in distilled water in contact with pure air but rusted if previously mechanically strained.

The following simple experiments throw some light on the mechanism of rusting.

EXPT. 1.—Take four lots, (*a*), (*b*), (*c*), (*d*), of clean iron nails.

(*a*) Boil ordinary tap-water in a test-tube until it begins to " bump," showing that dissolved air has been expelled. Drop the nails (*a*) into the water and boil again for half a minute. Pour melted vaseline over the surface of the water. This excludes air, so that iron and water alone are present (Hall, 1819; Adie, 1845).

(*b*) Place nails (*b*) in a test-tube full of ordinary water. In this case iron, much water, and air are present.

(*c*) Place nails (*c*) in a test-tube with a few drops of water. In this case iron, a little water, and air are present.

(*d*) Place nails (*d*) in a desiccator over sulphuric acid. In this case iron and air alone are present (Rinman, 1782).

Leave the four specimens for a few days, and examine the iron. Rusting should have occurred only in cases (*b*) and (*c*).

EXPT. 2.—Pour 100 c.c. of 15 p.c. caustic potash solution into a 500 c.c. flask fitted with a partly bored cork, and shake. Allow the flask to stand for two days. Boil a large bright nail with distilled water as described above (*a*), and push it through the cork into the flask, leaving a short length outside. Allow to stand for a few days. The part of the nail inside the flask which is exposed to air and water in the absence of carbon dioxide does not rust, whilst the part outside, exposed to moisture and ordinary air, will rust (G. A. Watson, *Nature*, 1907, **76**, 469; Patterson, *J.S.C.I.*, 1930, **49**, 203T.). In a modification of the experiment (Friend, *Proc. C.S.*, 1910, **26**, 179) liquid water is condensed on the iron, when rusting still does not occur.

EXPT. 3.—It will be noticed in Expt. 1 (*b*) that the undersides of the nails remain bright and rust is deposited on the top exposed to air. This indicates that the iron passes into solution, and the solution is then oxidised by the air. Pack a number of bright nails tightly in a jar, cover them with a piece of hardened filter paper, and pour boiled distilled water into the jar. Rust is deposited *above* the filter paper (Moody).

Dunstan, Jowett and Golding (*J.C.S.*, 1905, **87**, 1548; 1911, **99**, 1835) confirmed Hall's old observation that iron does not rust in moist air above the dew-point and found that it rusts in moist oxygen in the absence of carbon dioxide. They assumed the reactions:

$$Fe + O_2 + H_2O = FeO + H_2O_2$$
$$Fe + H_2O_2 = FeO + H_2O$$
$$2FeO + H_2O_2 = 2FeO(OH).$$

They were unable to detect any H_2O_2 during rusting, but a *trace* is said to be formed by the action of iron amalgam on alkaline solutions (Schönbein; Wieland and Franke, 1920).

That atmospheric carbon dioxide is essential to rusting (which seems probable from Expt. 2) was already denied by Rinman in 1782; other work (Vernon, *Trans. Faraday Soc.*, 1935, **31**, 1668) is said to show that it actually retards rusting. Lambert (*J.C.S.*, 1905, **87**, 1548; 1911, **99**, 1835), who took rigid precautions to exclude carbon dioxide, found that homogeneous pure iron does not rust even in ordinary air and is passive to copper sulphate solution, but ordinary iron rusts even in the absence of carbon dioxide.

Those who reject the *specific* action of carbonic acid follow an *electrochemical theory* of rusting (Thenard, 1819): different parts of a piece of iron act as poles of voltaic cells and solution of metal occurs as a result of local action of voltaic couples (Whitney, *J.A.C.S.*, 1903, **25**, 394; Bancroft, *J. Phys. Chem.*, 1924, **28**, 785).

Iron powder reacts slowly with air-free water with evolution of hydrogen and formation of black Fe_3O_4, and some hydrogen is evolved even in aerated water (Bengough, Lee and Wormwell, *Proc. Roy. Soc.*, 1931, **134**, 308). In presence of oxygen hydrated ferric oxide is precipitated as rust.

Iron in presence of water may be supposed to react primarily as

$$Fe + 2H^{\cdot} + 2OH' = Fe^{\cdot\cdot} + 2OH' + H_2$$

and as the process is electrolytic the ferrous and hydroxide ions appear at two different points; by diffusion they react with precipitation of ferrous hydroxide, which is then oxidised by dissolved oxygen:

$$4Fe(OH)_2 + O_2 + 2H_2O = 4Fe(OH)_3.$$

The action of carbonic acid is then supposed to be due to its furnishing $H^{\cdot}$ ions, and the inhibiting effect of alkali to their removal.

The primary formation of ferrous and hydroxide ions is shown by the following experiment (Cushman, 1907).

EXPT. 4.—Prepare a 1½ p.c. solution of agar in hot water and add a little sodium chloride and phenolphthalein. Pour the solution over a clean plate of iron in a glass dish. The agar sets to a jelly. After some hours red patches appear, indicating the formation of alkali by electrolysis. If potassium ferricyanide and phenolphthalein are added to the agar and the hot solution (*ferroxyl indicator*) is poured over clean iron nails, the anodes become blue from reaction of ferricyanide with ferrous ions, and the cathodes red from the alkali formed.

Iron is protected from rusting by painting, or whitewashing with lime. Pipes are protected by heating and dipping into a solution of coal-tar pitch in coal-tar naphtha, when an impervious coating is formed (*Angus Smith's compound*). In *Barff's process* the iron is heated to redness and steam passed over it, when an adherent layer of ferroso-ferric oxide is formed. This is used in treating cans for fruit, etc., instead of tinning. The layer of oxide is removed by heating with water containing magnesium chloride, which explains the corrosive action of sea water on boilers.

Passive iron.—When a bright piece of iron is immersed in *concentrated* nitric acid there is a slight reaction which soon practically ceases. The iron then remains bright and does not seem to dissolve. It is then insoluble in dilute nitric acid, which rapidly dissolves ordinary iron, and does not precipitate copper from a solution of copper sulphate (Wenzel, 1782; Keir, 1790; Heathcote, *J.S.C.I.*, 1907, **26**, 899; Hedges, *J.C.S.*, 1928, 969). The iron is then said to be *passive*. Other metals, *e.g.* aluminium (p. 418) and chromium (p. 739), may become passive in suitable conditions.

Iron also becomes passive in solutions of chloric, iodic, arsenic, and chromic acids, silver nitrate and potassium permanganate, and by anodic oxidation. Dry nitrogen dioxide produces a more intense passivity than nitric acid. Passive

iron becomes active and soluble in dilute acids, or reactive with copper sulphate, when scratched, when touched with a piece of active iron under dilute sulphuric acid, by immersion in concentrated alkali, or by heating in hydrogen.

Faraday's (1836) suggestion that passivity is due to a " coat of oxide . . . so thin as not to be sensible " has been confirmed (U. R. Evans, *J.C.S.*, 1927, 1020; *Nature*, 1930, **126**, 130; *Metallic Corrosion Passivity and Protection*, 1937) by dissolving out the iron in iodine solution or by anodic electrolysis in salt solution, leaving the transparent skin of oxide (Fe_2O_3).

Salts and Ions of Iron

Iron readily dissolves in dilute hydrochloric or sulphuric acid, producing **ferrous salts**, the solutions of which contain the bivalent **ferrous ion**: $Fe + 2H^{\cdot} = Fe^{\cdot\cdot} + H_2$. In cold dilute nitric acid (s. g. 1·034) no gas is evolved, but ferrous and ammonium nitrates are formed:

$$4Fe + 10HNO_3 = 4Fe(NO_3)_2 + NH_4NO_3 + 3H_2O.$$

With nitric acid above 5 p.c., NO, N_2O and N_2 are evolved and at a concentration of 24 g./100 c.c. the ammonia and nitrogen are replaced by NO and NO_2 (Armstrong and Acworth, *J.C.S.*, 1877, **32**, 54; Whiteley and Hallimond, *J.S.C.I.*, 1918, **37**, 736 A.).

In warm dilute nitric acid iron dissolves to ferric nitrate with evolution of nitric oxide:

$$Fe + 4HNO_3 = Fe(NO_3)_3 + NO + 2H_2O.$$

Solutions containing ferrous ion are nearly colourless, usually with a green tinge due to traces of ferric ion $Fe^{\cdot\cdot\cdot}$. The ferrous ion is readily oxidised to the **ferric ion** $Fe^{\cdot\cdot\cdot}$ which is almost colourless, the yellow, red or brown colour of ordinary solutions of ferric salts being due to undissociated compound, basic compounds, or colloidal ferric hydroxide formed by hydrolysis. When mixed with concentrated nitric acid they become nearly colourless; with concentrated hydrochloric acid they become deep yellow, the colour of undissociated ferric chloride.

Ferrous salts are *oxidised* to ferric salts:

(i) by atmospheric oxygen in neutral solution, when insoluble basic ferric salts are precipitated:

$$4Fe^{\cdot\cdot} + O_2 + 2H_2O = 4Fe^{\cdot\cdot\cdot} + 4OH';$$

(ii) by chlorine (or aqua regia), bromine or iodine (when the reaction is reversible: Dawson and Spivey, *J.C.S.*, 1932, 1838):

$$2Fe^{\cdot\cdot} + Hal_2 = 2Fe^{\cdot\cdot\cdot} + 2Hal';$$

(iii) by boiling nitric acid:

$$3Fe^{\cdot\cdot} + HNO_3 + 3H^{\cdot} = 3Fe^{\cdot\cdot\cdot} + NO + 2H_2O;$$

(iv) by permanganate in acid solution:

$$5Fe^{\cdot\cdot} + MnO_4' + 8H^{\cdot} = 5Fe^{\cdot\cdot\cdot} + Mn^{\cdot\cdot} + 4H_2O;$$

(v) by dichromate in acid solution :

$$6Fe^{\cdot\cdot} + Cr_2O_7'' + 14H^{\cdot} = 6Fe^{\cdot\cdot\cdot} + 2Cr^{\cdot\cdot\cdot} + 7H_2O ;$$

(vi) by silver salts (the reaction is reversible : Tananeff, *Z. phys. Chem.*, 1925, **114**, 49 ; *Z. anorg. Chem.*, 1924, **136**, 193 ; Noyes and Brann, *J.A.C.S.*, 1912, **34**, 1016) :

$$Fe^{\cdot\cdot} + Ag^{\cdot} \rightleftharpoons Fe^{\cdot\cdot\cdot} + Ag.$$

Ferric salts are *reduced* to ferrous salts :

(i) by nascent hydrogen (*e.g.* zinc and dilute sulphuric acid) :

$$Fe^{\cdot\cdot\cdot} + H = Fe^{\cdot\cdot} + H^{\cdot} ;$$

(ii) by hydrogen sulphide or sulphides :

$$2Fe^{\cdot\cdot\cdot} + H_2S = 2Fe^{\cdot\cdot} + 2H^{\cdot} + S,$$
$$2Fe^{\cdot\cdot\cdot} + S'' = 2Fe^{\cdot\cdot} + S,$$

(iii) by sulphur dioxide :

$$2Fe^{\cdot\cdot\cdot} + SO_2 + 2H_2O = 2Fe^{\cdot\cdot} + SO_4'' + 4H^{\cdot} ;$$

(iv) by iodides : $2Fe^{\cdot\cdot\cdot} + 2I' \rightleftharpoons 2Fe^{\cdot\cdot} + I_2$;

(v) by stannous chloride :

$$2Fe^{\cdot\cdot\cdot} + Sn^{\cdot\cdot} = 2Fe^{\cdot\cdot} + Sn^{\cdot\cdot\cdot\cdot}.$$

Ferrous salts act as *catalysts* in many reactions, probably because of alternate oxidation and reduction of $Fe^{\cdot\cdot}$ and $Fe^{\cdot\cdot\cdot}$ ions, and hence function as oxygen-carriers, or else a higher oxide is formed and reduced. They catalyse many reactions of hydrogen peroxide (p. 682), the action of persulphates on iodides, the oxidation of stannous chloride by oxygen, and the photo-reduction of mercuric chloride by oxalic acid. They *retard* the action of nitric acid on metals.

Ferrous Compounds

Ferrous hydride FeH_2 is formed as a black unstable solid by the action of ferrous iodide on a solution of zinc ethyl in ether (Wanklyn and Carius, 1861) or the action of hydrogen on ferrous chloride and magnesium phenyl bromide in ether (Weichselfelder and Thiede, 1926).

Ferrous fluoride FeF_2 (tetragonal) is formed as a white powder on heating iron powder or anhydrous ferrous chloride in a stream of hydrogen fluoride. It forms green $FeF_2,4H_2O$ and complex salts K_2FeF_4, $KFeF_3,2H_2O$ (pink), $NH_4FeF_3,2H_2O$ (green), etc.

Ferrous chloride $FeCl_2$ is obtained anhydrous in white (or grey) lustrous scaly hexagonal crystals, m.p. 670°, on heating iron in a stream of dry hydrogen chloride : $Fe + 2HCl = FeCl_2 + H_2$, or ferric chloride in hydrogen : $2FeCl_3 + H_2 = 2FeCl_2 + 2HCl$, or by evaporating a solution of ferrous chloride and ammonium chloride to dryness in absence of air and heating to volatilise the ammonium chloride. Solutions of iron in hydrochloric acid deposit on evaporation bluish-green monoclinic crystals of $FeCl_2,4H_2O$, which oxidise slightly in air and become green : on heating them in hydrogen chloride anhydrous $FeCl_2$ is formed. Other hydrates contain 1, 2 and 6 H_2O.

Anhydrous ferrous chloride volatilises at about 1000° and the vapour density indicates dissociation: $Fe_2Cl_4 \rightleftharpoons 2FeCl_2$, complete at 1300°–1500°. It oxidises on heating in air: $12FeCl_2 + 3O_2 = 2Fe_2O_3 + 8FeCl_3$, and in steam: $3FeCl_2 + 4H_2O = Fe_3O_4 + 6HCl + H_2$. The anhydrous compound dissolves in alcohol and ether. Ferrous and ammonium chlorides form only solid solutions (Clendinnen, *J.C.S.*, 1922, **121**, 801) but several double salts are formed with rubidium and caesium chlorides, *e.g.* $RbFeCl_3,2H_2O$ and $Cs_2FeCl_4,2H_2O$.

Ferrous bromide $FeBr_2$ and **ferrous iodide** FeI_2 are prepared from the elements and form the crystalline hydrates $FeBr_2,6H_2O$ (also with 2, 4 and 9 H_2O) and FeI_2,4 and 6 H_2O, which are formed by adding the halogen to excess of iron filings and water and evaporating. With excess of iodine a *ferrosoferric iodide* Fe_3I_8 is stated to be formed, but this is probably a mixture of ferrous iodide and free iodine.

Ferrous oxide FeO is formed as a black pyrophoric powder on heating ferric oxide in hydrogen at 300° or in a mixture of equal volumes of CO and CO_2 at 800°; by heating ferrous oxalate in absence of air at 150°–169°: $FeC_2O_4 = FeO + CO + CO_2$; by fusing Fe_3O_4 and iron; and by boiling ferrous oxalate with potassium hydroxide solution.

Pure FeO is unknown, as it always contains iron or Fe_3O_4; a nearly pure product is formed by heating at 700° small quantities (0·1 g.) of Fe_2O_3 in a mixture of steam and hydrogen in the ratio $H_2O : H_2 = 0{\cdot}58$ (Schenck and Dingmann, 1927).

Ferrous oxide crystallises in a rock-salt cubic lattice. It melts at 1355° and is reduced by hydrogen to iron at 700°–800°. It is not strongly magnetic. It reacts with a solution of chlorine in CCl_4: $6FeO + 3Cl_2 = 2Fe_2O_3 + 2FeCl_3$.

Ferrous hydroxide $Fe(OH)_2$, which crystallises in green rhombohedra with a brucite lattice (p. 365), is formed as a powdery white precipitate when alkali hydroxide is added to a ferrous salt solution in absolute exclusion of oxygen; the precipitate is usually green (perhaps basic ferrous ferrite, $HO{\cdot}Fe{\cdot}O{\cdot}Fe(OH)_2$). The solubility is $6{\cdot}7 \times 10^{-5}$ mol/lit. Flat green crystals are formed from a hot solution in very concentrated sodium hydroxide solution. Ferrous hydroxide rapidly oxidises to ferric hydroxide in air and is a powerful reducing agent; in alkaline solution it reduces hydroxylamine, nitric oxide, nitrites and nitrates to ammonia, and even perchlorate to chloride. It dissolves in very concentrated alkali hydroxide, perhaps forming a *ferrosite* (see p. 857) FeO_2'', and readily in acids forming ferrous salts.

Ferrous carbonate $FeCO_3$ occurs as *siderite* or *spathic iron ore* in rhombohedra isomorphous with calcite and with the same lattice (p. 243). It is formed on addition of alkali carbonate to a ferrous salt solution as a white precipitate rapidly becoming green and finally brown on exposure to air, owing to oxidation to ferric hydroxide. The solubility is about 10^{-5} mol/lit. It dissolves in water containing carbonic acid to form **ferrous bicarbonate** $Fe(HCO_3)_2$ and on exposure to air the solution deposits red ferric hydroxide (p. 675). Precipitated ferrous carbonate is soluble in ammonium carbonate solution.

Potassium ferrous carbonate $K_2[Fe(CO_3)_2],4H_2O$ is deposited in nearly white scales from a mixture of potassium carbonate solution and one-fifth of its volume of saturated ferrous chloride solution ; the precipitate first formed redissolves to a green solution which then crystallises (Reynolds, *J.C.S.*, 1898, **73**, 262).

Calcium ferrous carbonate $Ca[Fe(CO_3)_2]$ occurs impure in hexagonal crystals as *ankerite* in coal measures.

Ferrous nitrate is not easily made by dissolving iron in nitric acid (p. 849) and is best prepared by grinding ferrous sulphate and lead nitrate with dilute alcohol, filtering and evaporating : $FeSO_4 + Pb(NO_3)_2 = Fe(NO_3)_2 + PbSO_4$. Light green rhombic crystals of $Fe(NO_3)_2,6H_2O$ are formed ; the hydrate with $9H_2O$ is formed below $-12°$.

Ferrous phosphate $Fe_3(PO_4)_2,8H_2O$ occurs as *vivianite* in blue monoclinic crystals. It is colourless when obtained pure by precipitating ferrous sulphate solution with sodium phosphate and allowing to stand at 60°–80° (Carter and Hartshorne, *J.C.S.*, 1926, 363), but becomes blue in air from partial oxidation. The **acid phosphates** $FeHPO_4,H_2O$ and $2H_2O$, and $Fe(H_2PO_4)_2,2H_2O$, and a crystalline *nitroso-compound* $[Fe(NO)]HPO_4$ (Manchot, 1914), are known. There are two **iron phosphides** Fe_3P and Fe_2P.

Ferrous sulphide occurs native as the ferromagnetic reddish-bronze coloured *pyrrhotite* or *magnetic pyrites*, hexagonal, s. g. 4·5–5·0, m.p. 1180°. The composition, like that of the artificial sulphide, is never exactly FeS but there is always a defect of iron, the formula varying from Fe_7S_8 to Fe_8S_9. (The paramagnetic *troilite* found in most iron meteorites is said to have the exact formula FeS.)

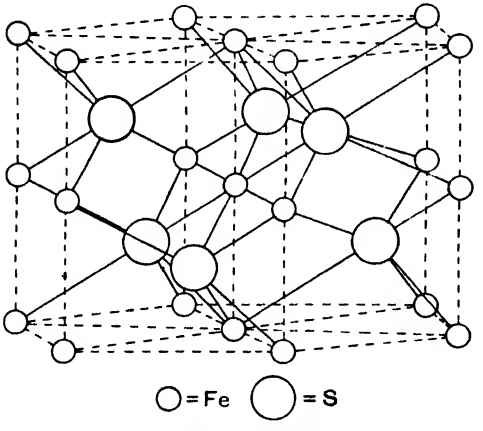


FIG. 339.—Ferrous sulphide lattice.

The sulphur atoms form nearly regular tetrahedra not containing any iron atom, and each iron atom is surrounded by six sulphur atoms at the corners of a slightly distorted octahedron (Fig. 339) (Harold. sen, *Z. anorg. Chem.*, 1941, **246**, 169, 195). The easy replacement of iron by sulphur (giving excess over FeS) may be due to a tendency to form S_2 radicals (present in iron pyrites FeS_2) (Goldschmidt, *Ber.*, 1927, **60**, 1263).

Iron filings burn when sprinkled into sulphur vapour, and a mixture of iron filings and powdered sulphur reacts with incandescence when heated. Ferrous sulphide is also formed by dipping a white-hot bar of wrought iron into melted sulphur in a crucible (cast iron does not react) ; this is dark grey or black and contains some free iron. Crystals are formed on heating iron to dull redness in hydrogen sulphide.

Ordinary ferrous sulphide is made by projecting by degrees a mixture of 30 pts. of iron filings and 21 pts. of flowers of sulphur into a red-hot crucible; the fused mass is allowed to cool and broken into pieces. The purest form is obtained as a yellowish crystalline mass with a metallic lustre by heating sulphur with twice its weight of iron, mixing the product with more sulphur and heating in a current of hydrogen (Jellinek and Zakowski, 1925). A mixture of iron filings and sulphur when moistened becomes hot and forms ferrous sulphide. An " artificial volcano " is formed by burying a large mass of the mixture (Lemery's experiment).

A greenish-black precipitate of ferrous sulphide is formed on adding ammonia and ammonium sulphide to a ferrous salt solution, or passing hydrogen sulphide into ferrous sulphate solution containing sodium acetate. It is insoluble in alkali but dissolves slightly in excess of yellow ammonium sulphide, forming a greenish-black solution probably containing a ferrisulphide NH_4FeS_2. Ferrous sulphide dissolves readily (except when pure) in dilute sulphuric or hydrochloric acid, evolving hydrogen sulphide (p. 694). It is decomposed by steam at a red heat: $3FeS + 4H_2O = Fe_3O_4 + 3H_2S + H_2$.

Iron disulphide FeS_2 occurs as golden-yellow cubic *pyrites* (s. g. 5·1), usually crystallising in cubes, plain or striated (more than 200 forms are described), and pale bronze-yellow or tin-white rhombic *marcasite* (s. g. 4·88), usually crystallising in radiating nodules or complicated twinned forms (" cock's comb-pyrites " or " spear-pyrites "). It contains *ferrous* iron and has long been formulated  .

The X-rays show that each sulphur atom is surrounded tetrahedrally by three iron atoms and another sulphur atom, with all of which it forms covalent bonds: FeS_2 is a derivative of H_2S_2 and is only slightly paramagnetic.

Both pyrites and marcasite are hard, striking sparks from steel, non-magnetic and insoluble in dilute acids but soluble in concentrated nitric acid or aqua regia. Pyrites is said to be formed from marcasite above 450° and is stable in moist air, but marcasite oxidises to an efflorescence of ferrous sulphate. Pyrites often occurs in coal and is found in the form of roots, wood, etc., probably formed by reduction of ferrous sulphate solution by vegetable matter. Pyrites crystals are formed by passing hydrogen sulphide over red-hot ferric oxide or chloride, or by heating a mixture of ferric oxide, sulphur and ammonium chloride.

Ferrous sulphate $FeSO_4$, the commonest ferrous salt, is obtained by dissolving iron in dilute sulphuric acid, by the slow oxidation of marcasite in moist air (pyrites is stable in air unless first roasted), and as a by-product in the preparation of hydrogen sulphide from ferrous sulphide and dilute sulphuric acid. The common form is *green vitriol* or *copperas* $FeSO_4,7H_2O$, monoclinic green crystals, m.p. 64°, isomorphous with one form of Epsom salt $MgSO_4,7H_2O$.

A crystal of white vitriol $ZnSO_4,7H_2O$ induces the deposition of isomorphous rhombic crystals of $FeSO_4,7H_2O$, whilst a crystal of blue vitriol $CuSO_4,5H_2O$ induces the deposition of triclinic crystals containing $FeSO_4,5H_2O$.

The pure salt $FeSO_4,7H_2O$, obtained by powdering and pressing between filter paper, is pale greenish-blue. By precipitating the solution with alcohol, heating the heptahydrate in vacuum at 140°, or crystallising from 50 p.c. sulphuric acid, the white monohydrate $FeSO_4,H_2O$, stable in air, is obtained. At 300° in a current of hydrogen this gives white amorphous $FeSO_4$. This decomposes at a red heat: $2FeSO_4 = Fe_2O_3 + SO_3 + SO_2$.

Crystal hydrates with 7, 4, 2 and 1 H_2O are stable; those with 6, 5 and 3 H_2O are metastable. In contact with saturated solutions $FeSO_4,7H_2O$ is stable from $-7{\cdot}8°$ to $56{\cdot}6°$, $FeSO_4,4H_2O$ from $56{\cdot}6°$ to $64{\cdot}4°$, above which $FeSO_4,H_2O$ decreases in solubility with rise in temperature:

Temp.	0°	10°	15·25°	25·02°	35·07°	40·05°	60·01°	70·04°	90·13°
g. $FeSO_4$/100 g. H_2O	15·65	20·51	23·86	29·60	36·87	40·20	54·95	56·08	37·27
Solid phase	$FeSO_4,7H_2O$						$FeSO_4,4H_2O$	$FeSO_4,H_2O$	

Ferrous sulphate readily forms double salts with alkali metal sulphates, which belong to the group of isomorphous *schönites* or *picromerites* with the general formula $M^I_2M^{II}(SO_4)_2,6H_2O$, where M^I is K,Rb,Cs and NH_4, M^{II} is Cu,Mg,Zn,Cd,Mn,Fe,Co,Ni, and Se,Te and Cr may replace S. The most important is **ferrous ammonium sulphate** (*Mohr's salt*) $(NH_4)_2Fe(SO_4)_2,6H_2O$, which separates on cooling, in light bluish-green monoclinic crystals stable in air, when equimolecular amounts of ferrous and ammonium sulphates are dissolved to saturation in separate amounts of warm water and the filtered solutions mixed. It deposits as a nearly white powder on adding alcohol to the saturated solution (cf. $FeSO_4$). The solution is much less easily oxidised than one of ferrous sulphate and is used in volumetric analysis (a drop or two of dilute sulphuric acid is added to make a clear solution). The salt contains almost exactly one-seventh of its weight of ferrous iron. The solubility at 25° is 35·1 g. $(NH_4)_2Fe(SO_4)_2$ in 100 g. of water.

Ferrous aluminium sulphate $FeAl_2(SO_4)_4,24H_2O$ occurs as *halotrichite* or *feather alum*. Iron dissolves without evolution of gas in sulphur dioxide solution; the solution deposits colourless crystals of **ferrous sulphite** $FeSO_3,3H_2O$ and the solution contains **ferrous thiosulphate**: $2Fe + 3H_2SO_3 = FeSO_3 + FeS_2O_3 + 3H_2O$.

Ferric Compounds

As ferric oxide Fe_2O_3 is a much weaker base than ferrous oxide FeO, the ferric salts tend to hydrolyse in solution and no ferric carbonate is known; Fe_2O_3 can also act as a weakly acidic oxide, forming ferrites (sometimes called ferrates) such as $NaFeO_2$, and thus resembles Al_2O_3 and Cr_2O_3, which form aluminates and chromites.

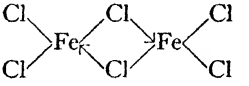
Ferric hydride FeH_3 is formed as a black unstable powder by the action of hydrogen on ferric chloride and magnesium phenyl bromide in ether (Weichselfelder and Thiede, 1926).

Ferric fluoride FeF_3, pale green or nearly white, is formed by the action of fluorine on iron. The pale rose-coloured hydrate $FeF_3,4{\cdot}5H_2O$ (or $[FeF_3(H_2O)_3]$, $1\frac{1}{2}H_2O$, as it loses $1\frac{1}{2}H_2O$ at 100° and is not ionised in solution) is formed by dissolving ferric hydroxide in hydrofluoric acid and evaporating. When strongly

heated in a stream of hydrogen fluoride it becomes anhydrous. Complex salts NH_4FeF_4, K_2FeF_5, K_3FeF_6, $CoFeF_5,7H_2O$, etc., are known. Na_3FeF_6 is sparingly soluble and the solution gives no red colour with thiocyanate.

Ferric chloride $FeCl_3$ sublimes in anhydrous iron-black hexagonal-rhombohedral crystals with a green iridescence, m.p. *c.* 300°, b.p. 315°, on heating iron (*e.g.* cuttings of iron wire) or (at 900°–1000°) ferric oxide in chlorine. It can be purified by sublimation in chlorine. The crystals volatilise at 280° and at 444° the vapour density corresponds with Fe_2Cl_6 (Deville and Troost, 1857). With rise of temperature the vapour density falls and at 750° it corresponds nearly with $FeCl_3$: $Fe_2Cl_6 \rightleftharpoons 2FeCl_3$. At high temperatures dissociation into $FeCl_2$ and Cl_2 may occur.

The formula Fe_2Cl_6 corresponds with the structure



analogous to that of aluminium chloride (p. 424). In boiling solutions in benzene, alcohol, ether, acetone and pyridine the molecular weight corresponds with $FeCl_3$; these, and solutions in aqueous hydrochloric acid, are bright yellow. A solution in aqueous alcohol is reduced by light and green crystals of $FeCl_2,2H_2O$ deposit. The solution in water is reduced by boiling with copper and hydrochloric acid to $FeCl_2$, cupric and cuprous chlorides being formed.

Ferric chloride solution is obtained by dissolving ferric hydroxide in hydrochloric acid or by saturating ferrous chloride solution with chlorine. On evaporation yellow readily soluble crystals of $FeCl_3,6H_2O$ or $Fe_2Cl_6,12H_2O$ deposit. Other hydrates contain Fe_2Cl_6 with 7, 5 and 4 H_2O (Fig. 340). The solution is strongly acid owing to hydrolysis: $FeCl_3 + 3H_2O \rightleftharpoons Fe(OH)_3 + 3HCl$, and the crystal hydrates lose hydrochloric acid on heating and leave a basic salt or ferric oxide. The only definite basic chloride is FeOCl. Garnet-red double salts are formed: *e.g.* Tl_2FeCl_5, K_2FeCl_5,H_2O, NH_4FeCl_4, etc. (Clendinnin, *J.C.S.*, 1923, **123**, 1338, 1634). Hydrates of the acid $HFeCl_4$ with 2, 4 and $6H_2O$ crystallise on cooling very concentrated solutions saturated with HCl.

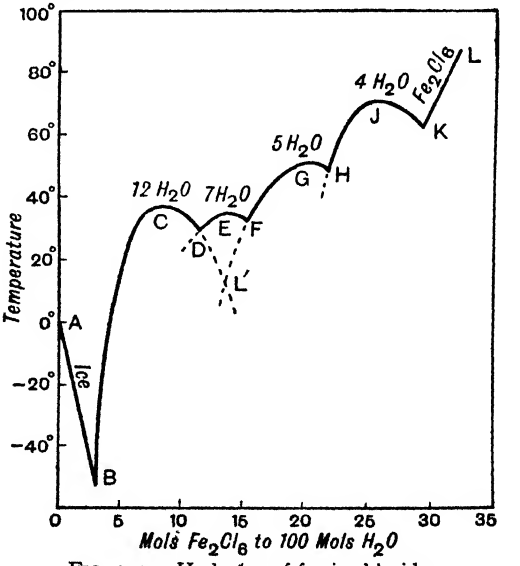


FIG. 340.—Hydrates of ferric chloride.

Ferric bromide $FeBr_3$ is formed similarly to the chloride, and forms green $FeBr_3,6H_2O$, but ferric iodide does not exist, as the iodide ion is oxidised by the ferric ion to iodine (p. 849).

Ferric oxide Fe_2O_3 exists in two common crystalline forms (Robbins, 1859; Malaguti, 1862), the rhombohedral paramagnetic *haematite* or α-Fe_2O_3, s. g. 5·1, and the cubic ferromagnetic γ-Fe_2O_3, s. g. 4·69 (cf. Al_2O_3, p. 420); a third dark brown ferromagnetic δ-Fe_2O_3 is obtained by oxidising ferrous sulphate with alkaline hydrogen peroxide (Glemser and Gwinner, 1939).

The common α-Fe_2O_3 is formed by a large number of reactions: igniting iron powder in air, or heating the precipitated hydroxide, lower oxides, ferrous sulphate or oxalate, ferric sulphate or nitrate, etc., and it becomes crystalline when strongly heated in a current of hydrogen chloride. The stable crystalline form is steel-grey but gives a red powder. All varieties (which have the same crystal structure) become brown to dark violet after heating at 650°–1000°, above this temperature bluish-black or grey, melting at 1563°; α-Fe_2O_3 gives off some oxygen at 1200° (Hostetter and Sosman, *J.A.C.S.*, 1916, **38**, 807, 1188). γ-Fe_2O_3 is said to lose some oxygen in vacuum at 250°.

Red varieties of α-Fe_2O_3 used as pigments or polishing powders (*rouge, crocus, colcothar*) are formed by igniting ferrous sulphate in air. When heated in presence of alumina, or calcium or barium sulphates, ferric oxide becomes *yellow*, and the brown and violet forms become yellowish-red by alternate grinding and washing. The ignited forms are nearly insoluble in acids but dissolve slowly in hot concentrated hydrochloric acid (more easily in presence of ferrous salt); a better solvent is a boiling mixture of 8 parts by weight of H_2SO_4 and 3 of water. Ferric oxide has catalytic activity (pp. 651, 707).

γ-Fe_2O_3 is metastable and passes into α-Fe_2O_3 with a velocity increasing with rise of temperature, the change being very slow below 400° and rapid at 700°. It is formed by dehydrating natural or artificial γ-FeO(OH), by oxidising natural or artificial Fe_3O_4 by heating in air, and by oxidising precipitated $Fe(OH)_2$ with alkaline H_2O_2 or precipitated $Fe_3(OH)_8$ with persulphate.

Ferric hydroxide also exists in several forms; definite crystalline varieties are Fe_2O_3,H_2O or FeO(OH). Two crystalline forms are the minerals *goethite* or α-FeO(OH), brownish-black, rhombic in columnar needles or radiating fibres, s. g. 4·28, paramagnetic susceptibility 29×10^{-6}; and *lepidocrocite* or γ-FeO(OH), red, rhombic in thin plates or leaves (indistinct), s. g. 4·09, paramagnetic susceptibility 42×10^{-6}.

What were once regarded as definite mineral hydrates: *hydro-haematite* or *turgite* (black) $2Fe_2O_3,H_2O$; *limonite* (brown) $2Fe_2O_3,3H_2O$; *xanthosiderite, ochre, hypoxanthite*, etc. (yellow to yellowish-brown) $Fe_2O_3,2H_2O$, and amorphous brownish-black *bog iron ore*, etc., $Fe_2O_3,3H_2O$, are FeO(OH) with Fe_2O_3 or adsorbed water.

Goethite or α-FeO(OH) is formed as a yellowish-brown precipitate by oxidising ferrous bicarbonate solution with hydrogen peroxide, oxidation of ferrous hydroxide or carbonate in presence of water by atmospheric oxygen, heating ferric hydroxide gel with dilute alkali in an autoclave, etc. On heating at 300° it forms α-Fe_2O_3.

Lepidocrocite or γ-FeO(OH) is obtained as a bright yellowish-red precipitate by warming a neutral or weakly acid ferrous solution with equivalent weights of sodium thiosulphate and potassium iodate, and by precipitating ferrous salts with alkaline hypochlorite ; it is also formed by oxidising precipitated ferrous hydroxide under special conditions. It loses water at 200°–250° to form γ-Fe_2O_3, which at higher temperatures forms α-Fe_2O_3.

An *amorphous* reddish-brown *gel* is precipitated from a ferric salt solution by ammonium chloride and ammonia ; it is slimy in the cold but becomes flocculent on boiling. It is soluble in dilute acids but practically insoluble in water (0·00015 g./lit. of $Fe(OH)_3$ at 20° : Almkvist, *Z. anorg. Chem.*, 1918, **103**, 240) and alkalis. On prolonged boiling in contact with the solution the precipitate forms α-FeO(OH) and becomes sparingly soluble in acids. The gel dries to a dark brown amorphous mass of indefinite composition which on heating loses water with production of a glow (p. 743 ; α-FeO(OH) does not glow on loss of water) and forms α-Fe_2O_3, nearly insoluble in acids.

A yellow β-FeO(OH) is said to be precipitated on heating ferric chloride solution (Weiser and Milligan, *J.A.C.S.*, 1935, **57**, 238). Some ferric hydroxide gels are *thixotropic*, *i.e.* become fluid on shaking and regelatinise on standing.

There are two forms of **colloidal ferric hydroxide sol** :

(i) *Graham's sol* (1861), deep blood-red and obtained by dissolving freshly precipitated ferric hydroxide in ferric chloride solution, or pouring ferric chloride solution into boiling distilled water, and dialysing, preferably hot. The sol (*dialysed iron*) so prepared is a positive colloid, readily precipitated by salts and by negative colloidal As_2S_3. (A negative sol is formed by adding ferric chloride solution to dilute NaOH solution.) Concentrated hydrochloric acid slowly converts it into a yellow solution of ferric chloride. A sol is also formed by oxidising $FeCl_2$ solution with $KMnO_4$ or H_2O_2 and dialysing (Neidle, etc., *J.A.C.S.*, 1916, **38**, 2607 ; 1917, **39**, 71).

(ii) *Péan de St. Gilles's sol* (1855), brick-red and formed by heating a solution of ferric acetate for several days, or dissolving freshly precipitated ferric hydroxide in acetic acid, diluting and boiling out the acetic acid.

Ferrites.—Ferric oxide is weakly acidic and with strong bases it forms **ferrites**, *e.g.* $NaFeO_2$ or $Na_2Fe_2O_4$ (sometimes called *perferrites* or *ferrates*, the ferrites being then the doubtful compounds of ferrous oxide, Na_2FeO_2, etc., p. 851 ; the name ferrate has also been given to a supposed $BaFeO_3$). An alkali ferrite is formed when iron (the reaction is slow) or precipitated ferric hydroxide dissolves in very concentrated alkali hydroxide solution : $2Fe + 2NaOH + 2H_2O = 2NaFeO_2 + 3H_2$, and $Fe(OH)_3 + NaOH = NaFeO_2 + 2H_2O$, and the solid is formed by fusing ferric oxide with alkali hydroxide : $Fe_2O_3 + 2NaOH = 2NaFeO_2 + H_2O$, or carbonate : $Fe_2O_3 + Na_2CO_3 = 2NaFeO_2 + CO_2$. This is decomposed by hot water : $2NaFeO_2 + H_2O = Fe_2O_3 + 2NaOH$, but with concentrated alkali hydroxide a solution of ferrite is obtained. Crystals of sodium ferrite are formed by boiling a solution of sodium ferrate (p. 860) and cooling :

$$4Na_2FeO_4 + 2H_2O = 4NaFeO_2 + 4NaOH + 3O_2.$$

Lithium ferrite has a rock-salt lattice of indistinguishable $Li^{\cdot}$ and $Fe^{\cdot\cdot\cdot}$ ions; **sodium ferrite** has a layer lattice of FeO_2' ions separated by $Na^{\cdot}$ ions. Ferrites of bivalent metals (Be, Mg, Ca, Sr, Ba, Zn, Cu, Pb, Mn, Fe, Co, Ni) are of the mixed oxide type $M^{II}O, Fe_2O_3$ with a spinel structure (p. 422). **Ferrous ferrite** $Fe^{II}Fe_2^{III}O_4$ is the important **ferrosoferric oxide** or *magnetic oxide of iron* Fe_3O_4.

Ferrosoferric oxide Fe_3O_4 occurs as cubic *magnetite*, which is ferromagnetic and often has magnetic polarity. It is formed (as " smithy scales ") by heating iron to redness in air, by burning iron in oxygen, heating iron to redness in steam (p. 283) or heating ferric oxide above 1000° in vacuum. Pure Fe_3O_4, s. g. 5·2, is formed as a black powder by passing hydrogen through water at 40° and passing the mixture of hydrogen and water vapour over ferric oxide at 400°: $3Fe_2O_3 + H_2 = 2Fe_3O_4 + H_2O$. Ferrosoferric oxide exists in only one form (Hedvall, 1922); it melts at 1540° and is cast into electrodes, as it is a good conductor and resists acids and chlorine.

Ferrosoferric hydroxide Fe_3O_4, aq., often formulated as $Fe<^{O—Fe(OH)_2}_{O—Fe(OH)_2}$ or $Fe_3(OH)_8$ (although this is only the theoretical equivalent of $Fe(OH)_2, 2Fe(OH)_3$ and the actual water content is smaller and variable), is formed as a black strongly magnetic powder (*martial aethiops*) by covering iron filings with water, exposing to air, and stirring frequently; also by adding a solution of ferrous and ferric salts in the ratio $Fe^{\cdot\cdot}/Fe^{\cdot\cdot\cdot} = 1 : 2$ to alkali hydroxide solution or boiling ammonia, washing and drying (Baudisch and Welo, *Phil. Mag.*, 1927, **3**, 396). It is soluble in hydrochloric acid and on evaporation over sulphuric acid yellow crystals separate, supposed to be $Fe_3Cl_8, 18H_2O$ but probably a mixture of ferrous and ferric chlorides.

Since $Fe(OH)_3$ is a very weak base, **ferric carbonate** is unknown, but green crystals of **basic ammonium ferrous ferricarbonate** $NH_4Fe_2^{II}[Fe^{III}(CO_3)_3(OH)_2], H_2O$ separate on atmospheric oxidation of a solution of ferrous carbonate in ammonium carbonate (Hauser, 1905).

Ferric nitrate is obtained by dissolving iron or ferric hydroxide in fairly concentrated nitric acid; the dark brown solution deposits colourless (usually pale violet) crystals of $Fe(NO_3)_3, 9H_2O$ (monoclinic), m.p. 40°, or $Fe(NO_3)_3, 6H_2O$ (cubic), m.p. 60·5°, from concentrated solutions (Lambert and Thomson, *J.C.S.*, 1910, **97**, 2426). The anhydrous salt is not known. The supposed basic nitrates are doubtful (Cameron and Robinson, *J. Phys. Chem.*, 1909, **13**, 251).

Ferric phosphate is formed as a white precipitate $FePO_4, 2H_2O$ on adding sodium phosphate to a ferric salt solution or ferric chloride to excess of phosphoric acid solution (Caven, *J.S.C.I.*, 1896, **15**, 17): it is soluble in dilute mineral acids (except phosphoric), but not in acetic acid, and is decomposed by boiling ammonia: $FePO_4 + 3NH_4OH \rightleftharpoons Fe(OH)_3 + (NH_4)_3PO_4$. Acid phosphates are $Fe_2O_3, 2P_2O_5, 8H_2O$ and $Fe_2O_3, 3P_2O_5, 6$ and $10H_2O$ (Carter and Hartshorne, *J.C.S.*, 1923, **123**, 2223; 1926, 363).

Ferric sulphide Fe_2S_3 is not formed from the elements but is obtained by the action of hydrogen sulphide at room temperature on *pure* moist ferric hydroxide in absence of oxygen (p. 458), and as a black precipitate by the action of excess of ammonia and ammonium sulphide on a solution of a ferric salt:

$2FeCl_3 + 3(NH_4)_2S = Fe_2S_3 + 6NH_4Cl$; with excess of ferric salt a mixture of FeS and sulphur is formed (Wright, *J.C.S.*, 1883, **43**, 156; Allen, Crenshaw and Johnston, *Amer. J. Sci.*, 1912, **33**, 169; Pearson and Robinson, *J.C.S.*, 1928, 814; Sayce, *ibid.*, 1929, 2002). It is dried in vacuum over P_2O_5 as it decomposes on heating: $Fe_2S_3 = FeS + FeS_2$. Ferric sulphide forms **thioferrites** $MFeS_2$ with alkali sulphides: $Fe_2S_3 + S'' = 2FeS_2'$. These are also formed from ferrous sulphide and alkali polysulphide: $2FeS + S_2'' = 2FeS_2'$. **Potassium thioferrite** $KFeS_2$ is formed in insoluble purple needles by fusing iron filings, sulphur and potassium carbonate and extracting with water; it is stable in air. On heating in hydrogen it forms black $K_2Fe_2^{II}S_3$ (also called a thioferrite). **Sodium thioferrite** $NaFeS_2,2H_2O$ is formed in violet-brown (or green) insoluble needles by fusing iron filings with sodium thiosulphate and extracting with water: it decomposes in air. With acids the salts evolve hydrogen sulphide and deposit sulphur: $2FeS_2' + 6H^{\cdot} = 2Fe^{\cdot\cdot} + 3H_2S + S$.

Ferric sulphate $Fe_2(SO_4)_3$ is formed as a yellowish-white powder by oxidation of ferrous sulphate by boiling with concentrated sulphuric acid (Fownes, 1844): $2FeSO_4 + 2H_2SO_4 = Fe_2(SO_4)_3 + SO_2 + 2H_2O$. The common violet-white crystals are rhombic but there is a rhombohedral form (Posnjak and Merwin, *J.A.C.S.*, 1922, **44**, 1965). On heating above 500° the salt decomposes reversibly (Bodenstein and Suzuki, 1910): $Fe_2(SO_4)_3 \rightleftharpoons Fe_2O_3 + 3SO_3$. It dissolves very slowly in water to a very concentrated solution; the rate of solution is much increased by ferrous sulphate or other reducing agent (cf. $CrCl_3$, p. 742). The solution is brown owing to hydrolysis but becomes paler on addition of sulphuric acid. Hydrates with 12, 10 (?), 9 (common, violet, hexagonal), 7, 6 and 3 H_2O are described. Basic salts, *e.g.* $2Fe_2O_3,5SO_3,17H_2O$ (occurring native as *copiapite*), and acid salts, *e.g.* $Fe_2O_3,4SO_3,9H_2O$, are known (Applebey and Wilkes, *J.C.S.*, 1922, **121**, 337; Posnjak and Merwin, *loc. cit.*). Ferric sulphate solution dissolves copper (Schluederberg, *J. Phys. Chem.*, 1908, **12**, 574).

Ferric sulphate forms **iron alums** $M^IFe(SO_4)_2,12H_2O$ where $M^I = K, NH_4$, Rb, Cs, Tl; these are violet when pure but are often pale yellow owing to the presence of ferric oxide (Rae, *J.C.S.*, 1916, **109**, 1331; Bonnell and Perman, *J.C.S.*, 1921, **119**, 1994). They are readily soluble and not appreciably hydrolysed. The ammonium alum crystallises more easily than the potassium; the Cs alum is sparingly soluble, and the Tl alum forms bright amethyst-red cubes. Rb and Cs ferric selenium alums $M^IFe(SeO_4)_2,12H_2O$ are pale violet.

Ferrates

Compounds containing 6-valent iron, the **ferrates** (sometimes called *perferrates*), discovered by Fremy in 1841, are derived from an unknown *iron trioxide* FeO_3 or *ferric acid* H_2FeO_4, and correspond with chromates and manganates:

$$K_2Fe^{VI}O_4 \qquad K_2Cr^{VI}O_4 \qquad K_2Mn^{VI}O_4$$

and K_2FeO_4 is isomorphous with K_2SO_4, K_2SeO_4, K_2CrO_4, K_2MnO_4 and K_2MoO_4. They are formed by heating iron with alkali nitrates or oxidising

ferric hydroxide in alkali with bromine. The sodium, potassium, calcium and magnesium salts are purple or very dark red, crystalline and soluble to deep red or violet solutions, fairly stable in presence of excess of alkali but slowly evolving oxygen and forming a precipitate of ferric hydroxide and a ferrite (*e.g.* $KFeO_2$) solution on dilution, rapidly on heating (p. 857) :

$$4FeO_4'' + 2H_2O = 4FeO_2' + 4OH' + 3O_2.$$

They are powerful oxidising agents but do not act on alcohol. The barium salt is sparingly soluble.

Potassium ferrate is formed slowly when iron filings are heated with potassium hydroxide with exposure to air, and rapidly with deflagration when a mixture of 1 pt. of iron filings and 2 pts. of potassium nitrate is thrown in small portions into a red-hot crucible : $Fe + 2KNO_3 = K_2FeO_4 + N_2 + O_2$. The mass dissolves in water to a purple solution, noticed by Stahl in 1703, and on addition of excess of solid potassium hydroxide deposits deep red crystals of K_2FeO_4. This is also formed by heating iron filings with potassium dioxide (KO_2), by the electrolysis of concentrated potassium hydroxide with a cast-iron anode, or by the action of chlorine or bromine on ferric hydroxide suspended in warm concentrated potassium hydroxide solution : $2Fe(OH)_3 + 10KOH + 3Br_2 = 2K_2FeO_4 + 6KBr + 8H_2O$. Barium chloride precipitates fairly stable carmine-red **barium ferrate** $BaFeO_4,H_2O$ from potassium ferrate solution ; it loses water at 108° and becomes green, and is decomposed by hydrochloric and nitric acids, but not by dilute sulphuric acid. **Calcium ferrate** $CaFeO_4$ is formed by adding ferric chloride solution to bleaching powder and boiling.

According to Goralevich (1926) a green **perferrate** K_2FeO_5 derived from FeO_4 is formed by fusing ferric oxide with potassium hydroxide and *excess* of potassium nitrate or chlorate : $Fe_2O_3 + 4KOH + 5KNO_3 = 2K_2FeO_5 + 5KNO_2 + 2H_2O$, or $2Fe_2O_3 + 8KOH + 12KClO_3 = 4K_2FeO_5 + 6KClO_4 + 6KCl + O_2 + 4H_2O$.

Cyanogen Compounds of Iron

Ferrous cyanide $Fe(CN)_2$ is formed in light green cubic crystals on heating ammonium ferrocyanide to 320° in vacuum : $(NH_4)_4Fe(CN)_6 = Fe(CN)_2 + 4NH_4CN$. It decomposes over 430°. The X-ray spectrum indicates that it is polymerised and is probably ferrous ferrocyanide $Fe_2[Fe(CN)_6]$ (Brill and Mark, *Z. phys. Chem.*, 1928, **133**, 443). **Ferric cyanide** $Fe(CN)_3$ is unknown : alkali cyanide precipitates only ferric hydroxide from a ferric salt solution :

$$Fe''' + 3CN' + 3H_2O = Fe(OH)_3 + 3HCN.$$

The complex **ferrocyanides** (or *cyanoferrites*) and **ferricyanides** (or *cyanoferrates*) containing the stable ions $Fe(CN)_6''''$ and $Fe(CN)_6'''$, respectively, are important compounds.

When nitrogenous organic matter such as horn-shavings, dried blood, or leather-clippings is fused with potassium carbonate and iron filings and the mass digested with water, the solution on evaporation deposits yellow crystals of **potassium ferrocyanide** or *yellow prussiate of potash*, $K_4Fe(CN)_6,3H_2O$. The solution gives with a ferric salt a deep blue precipitate of *Prussian blue*, the first cyanogen compound discovered (Diesbach, 1704). Macquer (1752) showed that potassium

ferrocyanide is formed on boiling Prussian blue with potash, and Porret (1814) discovered **hydroferrocyanic acid** $H_4Fe(CN)_6$, formed as a white precipitate on adding an acid and then ether to a ferrocyanide solution. The precipitate contains combined ether (Baeyer and Villiger, *Ber.*, 1901, **34**, 2679).

Potassium ferrocyanide is prepared from the spent oxide of gas works (p. 459), and by adding excess of potassium cyanide to a solution of ferrous sulphate until the brown precipitate redissolves. The crystals are yellow tetragonal pyramids, unchanged in air but on heating giving a white powder of anhydrous salt. Potassium ferrocyanide, it is said, is not poisonous. **Sodium ferrocyanide** $Na_4Fe(CN)_6.10H_2O$ is prepared in a similar manner. Silver nitrate gives a white precipitate of **silver ferrocyanide** $Ag_4Fe(CN)_6$. **Cupric ferrocyanide** $Cu_2Fe(CN)_6$ forms a brown gelatinous precipitate. Precipitates of $K_2Me^{II}Fe(CN)_6$ are formed by Mg, Ca, Ba and Hg-ic salts.

The **ferrocyanide ion** contains bivalent iron, as is seen from its valency $Fe(CN)_6''''$ $(2-6=-4)$. It can be oxidised by chlorine or electrolytically to the **ferricyanide ion** $Fe(CN)_6'''$ containing tervalent iron $(3-6=-3)$:

$$2Fe(CN)_6'''' + Cl_2 = 2Fe(CN)_6''' + 2Cl'.$$

This takes place when chlorine is passed into a solution of potassium ferrocyanide or over the powdered nearly anhydrous salt. (The reverse reaction occurs on warming ferricyanide with concentrated hydrochloric acid.) By repeated crystallisation the potassium chloride is separated and dark red monoclinic crystals of **potassium ferricyanide** (*red prussiate of potash*) are obtained (L. Gmelin, 1822). Potassium ferricyanide is also formed by oxidising the ferrocyanide in acid solution with bromate or permanganate. It is an oxidising agent, converting lead monoxide to dioxide and chromic hydroxide to chromate in boiling alkaline solution, and liberating iodine from iodide, when it is reduced to ferrocyanide:

$$2Fe(CN)_6''' + 2OH' = 2Fe(CN)_6'''' + O + H_2O$$
$$2K_3Fe(CN)_6 + 2KOH + PbO = 2K_4Fe(CN)_6 + PbO_2 + H_2O$$
$$3K_3Fe(CN)_6 + 5KOH + Cr(OH)_3 = 3K_4Fe(CN)_6 + K_2CrO_4 + 4H_2O.$$
$$2Fe(CN)_6''' + 2I' = 2Fe(CN)_6'''' + I_2.$$

An alkaline solution of ferricyanide is reduced to ferrocyanide by sodium amalgam, glucose, hydrogen peroxide, hydrogen sulphide, or hydrazine:

$$Fe(CN)_6''' + Na = Fe(CN)_6'''' + Na^{\cdot}$$
$$2Fe(CN)_6''' + H_2O_2 + 2OH' = 2Fe(CN)_6'''' + 2H_2O + O_2.$$
$$6K_3Fe(CN)_6 + 3H_2S = 4K_4Fe(CN)_6 + K_2Fe[Fe(CN)_6] + 6HCN + 3S.$$
$$4Fe(CN)_6''' + 4OH' + N_2H_4 = 4Fe(CN)_6'''' + N_2 + 4H_2O.$$

Potassium ferricyanide solution does not keep and should be freshly prepared from crystals previously washed with a little water to remove ferrocyanide.

Hydroferricyanic acid $H_3Fe(CN)_6$ is formed in brown needles on adding fuming hydrochloric acid to a cold saturated solution of potassium ferricyanide, or pure by decomposing lead ferricyanide by dilute sulphuric acid, filtering and evaporating.

Lead ferricyanide deposits in brown crystals $Pb_3[Fe(CN)_6]_2,16H_2O$ from a hot solution of lead nitrate and potassium ferricyanide. **Silver ferricyanide** $Ag_3Fe(CN)_6$ forms a red, and **cupric ferricyanide** $Cu_3[Fe(CN)_6]_2$ a greenish-brown, precipitate.

Complex iron cyanides.—In the following description, for economy of space, the cyanogen radical CN is denoted by Cy and the valency of the iron atom by primes ($Fe^{II} = Fe''$, $Fe^{III} = Fe'''$) as in the old formulae. The description is based mainly on the work of K. A. Hofmann and co-workers (1904–09); other experimenters sometimes report somewhat different results.

Addition of ferrous salt solution to cold *neutral* potassium ferrocyanide solution in absence of oxygen (*e.g.* if a little $Na_2S_2O_4$ is added) gives a white precipitate of **potassium ferrous ferrocyanide** (*Everitt's salt*) $K_2Fe''[Fe''Cy_6]$, rapidly oxidising in air to **β-soluble Prussian blue** or **potassium ferric ferrocyanide** $KFe'''[Fe''Cy_6]$, soluble in water but insoluble in oxalic acid. With *acid* ferrocyanide solution a white $K_2Fe''[Fe''Cy_6]$ is precipitated, less easily oxidised by air and forming **γ-soluble Prussian blue**, also $KFe'''[Fe''Cy_6]$ but more stable than the β-form towards acids, alkalis and ferric chloride. The pale yellow insoluble residue from the preparation of hydrocyanic acid by boiling potassium ferrocyanide with dilute sulphuric acid is also $K_2Fe''[Fe''Cy_6]$, formed by the reaction :

$$2K_4Fe(Cy)_6 + 3H_2SO_4 = K_2Fe''[Fe''Cy_6] + 3K_2SO_4 + 6HCy,$$

but this is much less easily oxidised than the other two forms : nitric acid or hydrogen peroxide converts it into a form of potassium ferric ferrocyanide called **Williamson's violet** $KFe'''[Fe''Cy_6],H_2O$. By heating a solution of hydroferrocyanic acid $H_4Fe(CN)_6$ in a sealed tube at 110°–120° a white precipitate of the acid $H_2Fe''[Fe''Cy_6]$ is formed, which on oxidation gives a violet substance, perhaps $HFe'''[Fe''Cy_6]$.

The precipitate from potassium ferrocyanide solution with rather less than the equivalent of ferric chloride, when washed by decantation with potassium chloride solution and then 70 p.c. alcohol, forms on drying over P_2O_5 **α-potassium ferric ferrocyanide** or **α-soluble Prussian blue**, with a bronze lustre and giving a beautiful blue powder. It dissolves in water to a blue colloidal solution and also in oxalic acid. It may be either $KFe'''[Fe''Cy_6]$ or $KFe''[Fe'''Cy_6]$, but as hydrogen peroxide, which reduces ferricyanides to ferrocyanides, oxidises ferrous ferrocyanides to Prussian blue, this probably contains ferric iron in the basic radical and the formula is $KFe'''[Fe''Cy_6]$. The same Prussian blue is formed by precipitating a ferricyanide with a ferrous salt and in this case $KFe''[Fe'''Cy_6]$ must undergo change into $KFe'''[Fe''Cy_6]$.

With excess of ferric chloride the precipitate becomes insoluble in water and is called **insoluble Prussian blue** ; it is **ferric ferrocyanide** $Fe_4'''[Fe''Cy_6]_3$ or Fe_7Cy_{18}, but contains water which cannot be driven off by heat and is generally formulated as $Fe_7Cy_{18},9H_2O$. It is the main constituent of ordinary Prussian blue.

The precipitate obtained by adding an excess of ferrous salt to potassium ferricyanide, called **Turnbull's blue**, is identical with insoluble Prussian blue. A ferric salt with potassium ferricyanide gives a deep brown solution but no precipitate. A little stannous chloride or granulated zinc and acid precipitate Prussian blue. If chlorine is passed into *boiling* potassium ferrocyanide solution in the dark, or Prussian blue is oxidised with dilute nitric acid, a green precipitate of **ferric ferricyanide** $Fe'''[Fe'''Cy_6]$, called **Berlin green**, is formed.

The structures of Prussian blue, Turnbull's blue and Berlin green are revealed by X-rays (Keggin and Miles, *Nature*, 1936, **137**, 577). The lattice of Prussian

blue or $KFe'''[Fe''(CN)_6]$ is cubic with ferrous and ferric atoms alternately at the corners and CN radicals on the edges, the K atoms being at the centres of alternate cubes (Fig. 341). Potassium ferrous ferrocyanide $K_2Fe''[Fe''(CN)_6]$

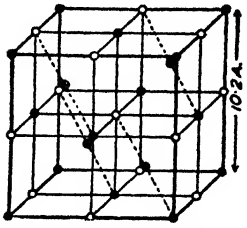


FIG. 341.—Lattice of Prussian blue $KFe[Fe(CN)_6]$.

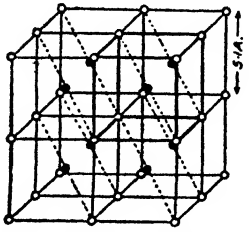


FIG. 342.—Lattice of potassium ferrous ferrocyanide $K_2Fe[Fe(CN)_6]$.

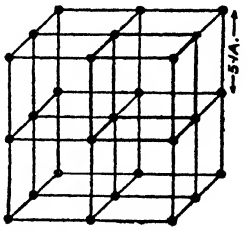


FIG. 343.—Lattice of Berlin green $Fe[Fe(CN)_6]$.

has a similar structure, but all the iron atoms are ferrous and hence to balance the charges a potassium atom is at the centre of every cube (Fig. 342). In Berlin green all the iron atoms are ferric and there are no alkali metal atoms in the lattice (Fig. 343). Ruthenium purple $KFe'''[Ru''(CN)_6]$ has a similar structure to Prussian blue $KFe'''[Fe''(CN)_6]$

Nitroso-salts of iron.—Potassium ferrocyanide warmed with 50 p.c. nitric acid gives a brown solution. When a slate-coloured precipitate is formed with ferrous sulphate the liquid is cooled, separated from the crystals of potassium nitrate and neutralised with sodium carbonate. The filtered solution on evaporation gives red rhombic crystals of **sodium nitroprusside** (Playfair, 1849), $Na_2[Fe(NO)(CN)_5],2H_2O$, which may be freed from nitrate by repeated crystallisation :

$$3H_4Fe(CN)_6 + HNO_3 = 3H_3Fe(CN)_6 + NO + 2H_2O$$
$$Fe(CN)_6''' + NO = Fe(CN)_5(NO)'' + CN'.$$

A nitroprusside is formed on passing NO into acidified ferricyanide solution.

A freshly prepared solution of sodium nitroprusside (it decomposes on standing) gives with alkali sulphides but not with free hydrogen sulphide an intense purple colour (Gmelin, 1848, with a crude nitroprusside solution), perhaps due to $[Fe(O{:}N{\cdot}S)(CN)_5]'''' : Fe(CN)_5(NO)'' + S'' = Fe(CN)_5(NOS)''''$. With alkali a nitroprusside forms a red **nitritoferrocyanide**, *e.g.* $Na_4[Fe(CN)_5(NO_2)],10H_2O$: $Fe(CN)_5(NO)'' + 2OH' = Fe(CN)_5(NO_2)'''' + H_2O$. With alkali sulphite a nitroprusside gives a rose-red colour (Boedeker, 1861) and a pale yellow salt with the formula $Na_5[Fe(CN)_5SO_3],9H_2O$ is formed.

Silver nitrate gives with sodium nitroprusside a flesh-coloured precipitate of $Ag_2[Fe(CN)_5(NO)]$ and by reaction of this with hydrochloric acid the unstable free acid $H_2[Fe(NO)(CN)_5]$ is formed.

The nitroprussides were usually considered to contain ferric iron and the neutral NO molecule, $Fe^{III}(Cy_5NO)$ giving the valency $3 - 5 = -2$, but Pauling (*J.A.C.S.*, 1931, **53**, 3225 ; Sidgwick and Bailey, *Proc. Roy. Soc.*, 1934, **144**, 521) suggested that the odd electron of the NO molecule . : N : : : O : enters the valency shell of the ferric ion in K_3FeCy_6, forming a *ferrous* ion, and the : N : : : O : radical then coordinates by the electron pair on the nitrogen. This gives the valency $2 - 5 + 1 = -2$, since the (NO) has now become positively univalent,

The formulation with ferrous iron agrees with the diamagnetism of the nitroprusside (K_3FeCy_6 is paramagnetic).

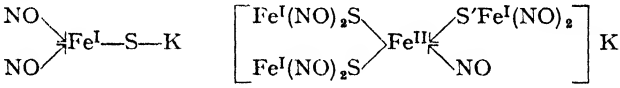
Potassium carbonyl ferrocyanide $K_3Fe(CN)_5CO$ is formed on passing moist CO over potassium ferrocyanide at 130° :

$$K_4Fe(CN)_6 + CO + 2H_2O = K_3Fe(CN)_5CO + NH_3 + H{\cdot}COOK.$$

It is very stable and only slightly oxidised by ozone and permanganate. The free acid and other salts are known.

If a solution of ferrous sulphate in excess of a thiosulphate is saturated with nitric oxide, **iron dinitroso-thiosulphates** are formed, *e.g.* reddish-brown leaflets of $K[FeS_2O_3(NO)_2],H_2O$, or brilliant jet-black crystals of $Rb[FeS_2O_3(NO)_2],H_2O$. If nitric oxide is passed into a suspension of precipitated ferrous sulphide in dilute alkali sulphide solution, or ferrous sulphate acts on a mixture of alkali nitrite and sulphide, *black Roussin's salts* are formed, *e.g.* $KFe_4(NO)_7S_3$, which form dark brown solutions with water. By the action of boiling dilute alkalis on these, *red Roussin's salts* such as $KFe(NO)_2S,2H_2O$ are formed.

Manchot (1926–31) supposed that the Roussin salts contain *univalent* iron, the NO functioning as a neutral molecule :



Ferric thiocyanate $Fe(CNS)_3$ is formed in the deep red solution produced on adding an alkali thiocyanate to a ferric salt solution. The red colour is soluble in ether. It has been supposed that the colour is due to a complex ion $Fe(CNS)_6'''$ or $Fe(CNS)^{\cdot\cdot}$. On dilution the colour fades, owing to reduction. (Philip and Bramley, *J.C.S.*, 1913, **103**, 795 ; Schlesinger and von Falkenburg, *J.A.C.S.*, 1931, **53**, 1212 ; Bent and French, *ibid.*, 1941, **63**, 568 ; Schlesinger, *ibid.*, 1765.)

Cobalt

Some specimens of ancient Egyptian (1375 B.C.) and Babylonian (1450 B.C.) blue glazes and glass contain cobalt, but most ancient blue glazes contain a copper calcium silicate $CaO,CuO,4SiO_2$. Some specimens of Roman blue glass (*e.g.* a piece found at Uriconium) contain cobalt.

Native cobalt arsenide $CoAs_2$ was called *cobalt* by the old German miners of the Harz (a *kobold* is a mine goblin) ; on roasting it gave *zaffre* (probably derived from " sapphire ") or impure cobalt arsenate, which when fused with sand and potassium carbonate gave a beautiful blue glass called *smalt*, containing the dark blue crystalline potassium cobalt silicate $K_2O,CoO,3SiO_2$ (Duboin, 1921). Metallic cobalt (*cobalt rex*) was obtained by Brandt in 1735 and was studied by Bergman in 1780.

Cobalt is rather rarer than nickel, with which it is nearly always found. It occurs native in small amounts and is found in meteorites. Its chief ores are *smaltite* or *speiss cobalt* $CoAs_2$ or $(Co,Ni,Fe)As_2$, *linnaeite* $(Co,Ni,Fe)_3S_4$, *cobaltite* or *cobalt glance* (Co,Fe)AsS, and *erythrite* or *cobalt bloom* $Co_3(AsO_4)_2$, $8H_2O$. Cobalt is now mainly obtained from the copper ores of Rhodesia and Katanga, and from the arsenides and sulphides in the silver ores of Cobalt City, Ontario. The cobalt glance of Queensland (Australia) is important,

and the New Caledonian manganese ore *asbolite* (a psilomelane, p. 820) contains about 1·6 p.c. of cobalt.

The Canadian ore is roasted to free it from arsenic and sulphur and fused in a blast-furnace with limestone and sand to form a flux. The iron passes into the slag and impure cobalt and nickel arsenide and antimonide settle out as *speiss*. This is ground and roasted to drive off most of the arsenic (and antimony if present), and the residue roasted with salt. Silver, if present, is extracted by cyanide. The residue is boiled with concentrated sulphuric acid and the " sulphated speiss " is agitated with water. Iron, arsenic and antimony are precipitated with limestone, copper from the filtrate by sodium carbonate, and the cobalt is precipitated as peroxide by sodium hypochlorite. Nickel in the filtrate is precipitated by sodium carbonate as basic carbonate, the last portion as peroxide by sodium hypochlorite (Gant, *J.S.C.I.*, 1925, **44**, 157, 191).

The cobalt oxide (usually Co_3O_4) is used as such or mostly made into cobalt compounds. The calcined oxide should contain 71–75 p.c. of cobalt and less than 1 p.c. of nickel. The metal may be obtained by reducing the oxide with carbon and limestone in the electric furnace, and usually contains about 1 p.c. of carbon and 0·015 p.c. of sulphur. The pure metal may be prepared by electrolysis of a solution of the sulphate containing ammonium sulphate and ammonia (Kalmus, *Ind. Eng. Chem.*, 1915, **7**, 6, 379). The purification of cobalt from nickel is best done by precipitation as the cobaltammine $[Co(NH_3)_5Cl]Cl_2$ (Claudet, 1851 ; Morgan and Smith, *J.S.C.I.*, 1924, **43**, 1317). The last trace of nickel is precipitated with dimethylglyoxime.

Cobalt is tenacious, silver white with a bluish cast which nickel has not, is readily polished and has a high lustre. It is ferromagnetic up to 1100°. Electrodeposited cobalt has a close-packed hexagonal structure ; above 400° it forms the ordinary face-centred cubic cobalt, but not completely.

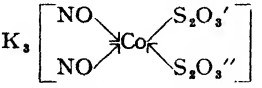
Cobalt slowly oxidises when heated in air and when finely divided is pyrophoric. It absorbs 59–153 vols. of hydrogen when finely divided. The metal dissolves slowly in concentrated hydrochloric and dilute sulphuric acids and readily in 50 p.c. nitric acid. It becomes passive in *cooled* fuming nitric acid, especially if superficially oxidised by heating in air.

Cobalt steel (35 p.c. Co) was used for permanent magnets of magnetos, as these can be made much smaller than carbon steel magnets, and do not become demagnetised. A nickel-aluminium steel with more than twice the coercivity of cobalt steel is now used instead. *Stellite* is an alloy of chromium and cobalt and a little tungsten, very hard and non-corroding, and used for surgical instruments. *Festel metal* or *cochrome* is an alloy of iron, chromium and cobalt used for cutlery or for electric heating elements.

Cobalt Compounds

Cobalt in its compounds has valencies of 1, 2, 3 and (in impure CoO_2) 4. The commonest are the **cobaltous compounds** of bivalent cobalt ; there are a few simple **cobaltic compounds**, and very many complex compounds, of tervalent cobalt. The soluble cobaltous compounds form pink solutions probably containing the hydrated ion $[Co(H_2O)_4]^{\cdot\cdot}$, since the coordination number of Co^{II} is 4. The coordination number of Co^{III} is 6.

Univalent cobalt is reported (Manchot, 1926) in the compound:



and a complex ion $[Co^{I}(CN)_4]$ is present in a brownish-green solution, evolving hydrogen at room temperature, formed by reducing a solution of $K_3[Co(CN)_6]$ with potassium amalgam or electrolytically (Grube, 1926).

Cobaltous Compounds

Black **cobaltous hydride** CoH_2 is formed by passing hydrogen into an ether solution of phenyl magnesium bromide containing $CoCl_2$ (Weichselfelder and Thiede, 1926).

Cobaltous fluoride CoF_2, tetragonal, m.p. 1250°, formed by heating $CoCl_2$ in a current of HF, the hydrate $CoF_2,4H_2O$ and double salts, $KCoF_3$ and $(NH_4)_2CoF_4,2H_2O$, are all red (cf. $CoCl_2$).

Cobaltous chloride $CoCl_2$, m.p. 735°, b.p. 1049°, sublimes in blue rhombohedral crystals, isomorphous with cadmium chloride $CdCl_2$, when cobalt is heated in chlorine, and is formed as a blue mass by heating any of the hydrates at 140°. The common hydrate $CoCl_2,6H_2O$ is formed in dark red deliquescent monoclinic crystals, m.p. 86°, from a solution of cobalt or the oxide or carbonate in hydrochloric acid. The lower hydrates with 2 and $1H_2O$ are violet. The pink solution of cobaltous chloride becomes blue on heating above 50° or addition of concentrated hydrochloric acid (which may precipitate the di- or monohydrates or $CoCl_2$) or concentrated sulphuric acid, and the solid hydrate gives a bluish-purple solution with alcohol. (Cobaltous nitrate solution becomes blue with concentrated hydrochloric acid but not with concentrated sulphuric acid).

A solution of cobalt chloride is a *sympathetic ink*; the writing is almost invisible but becomes blue on warming the paper before a fire. On standing in moist air the colour disappears.

The old theory (von Babo, 1857; Gladstone, 1858) that the colour changes are due to different degrees of hydration has been revived in a modified form (Howell, *J.C.S.*, 1927–36; *Proc. Roy. Soc.*, 1936, **155**, 33, bibl.), but the usually accepted view is that the blue colour in solutions is due to complex anions: $2CoCl_2 \rightleftharpoons Co^{\cdot\cdot} + CoCl_4''$ (Donnan and Bassett, *J.C.S.*, 1902, **81**, 939, bibl.; Bassett and Croucher, *J.C.S.*, 1930, 1784, bibl.; Percival and Wardlaw, *J.C.S.*, 1929, 1505). The ion $CoCl_4''$ was shown to migrate to the anode on electrolysis. The salt Cs_3CoCl_5 contains $Cs^{\cdot}$, Cl' and $CoCl_4''$ (tetrahedral) ions (Powell and Wells, *J.C.S.*, 1935, 359).

Cobaltous bromide (hexagonal) $CoBr_2$, obtained by adding bromine to cobalt powder in ether and heating the $CoBr_2,Et_2O$ formed, is dark green; it forms hydrates with 6 (dark red), 5 (violet-red) and 2 (purple) H_2O. **Cobaltous iodide** (hexagonal) CoI_2, which is black, obtained by heating cobalt in iodine vapour, and the hydrates with 9 (light red), 6 (dark red), and 2 (green) H_2O are very deliquescent.

Cobaltous oxide CoO, an olive-green powder and octahedral crystals with a rock-salt cubic lattice, is formed by heating the hydroxide, by passing steam over red-hot cobalt: $Co + H_2O \rightleftharpoons CoO + H_2$ (cf. Fe and Ni), and by *strongly* heating the carbonate or nitrate out of contact with air. It is stable at 1000°, but when heated in air forms Co_3O_4. It dissolves in acids to form cobaltous salts, and with magnesium, zinc and aluminium oxides forms **cobaltites** which are pink, green and blue, respectively. A blue solution of potassium cobaltite is formed from a cobalt anode in potassium hydroxide solution.

A solution of cobalt nitrate is used in blowpipe analysis. The ignited residue on charcoal is moistened with one drop of dilute cobalt nitrate and reheated. Zinc gives a *green* mass (*Rinman's green*, a solid solution), aluminium a *blue* mass (*Thenard's blue*, Al_2CoO_4), although blue masses are also produced with phosphates. Magnesia gives a pink mass, a solid solution. The compounds $4CoO,3Al_2O_3$, Co_2SnO_4 and $CoCr_2O_4$ are green. Cobalt salts give a beautiful blue borax bead.

Cobaltous hydroxide $Co(OH)_2$ precipitated by alkali hydroxide from a cobaltous salt solution is first bluish-violet, but forms a pink powder on standing in presence of excess of alkali, more rapidly on boiling. The blue and pink varieties are different crystalline forms, the pink having a brucite $Mg(OH)_2$ lattice (p. 365). The moist hydroxide absorbs oxygen from air and forms brown Co_3O_4. The solubility is 0·0032 g./lit. at 20°. It dissolves in hot concentrated potassium hydroxide and separates on cooling as a violet crystalline powder.

Cobaltous carbonate $CoCO_3$ is rhombohedral and isomorphous with calcite. The hydrate $CoCO_3,6H_2O$ is formed on standing as a pink precipitate from a cold solution of a cobaltous salt and sodium bicarbonate saturated with carbon dioxide; the precipitates with alkali carbonate or bicarbonate contains cobaltous hydroxide. Cobalt carbonate forms pink $K_2Co(CO_3)_2,4H_2O$ and bright reddish-purple $Na_2Co(CO_3)_2,4H_2O$ (Applebey and Lane, *J.C.S.*, 1918, **113**, 609).

Cobaltous nitrate $Co(NO_3)_2,6H_2O$ is formed in pink slightly deliquescent monoclinic crystals from a solution of the metal, oxide or carbonate in dilute nitric acid. There are also hydrates with 9 and $3H_2O$. The slightly pink anhydrous salt is formed (Guntz and Martin, 1909) by the action of concentrated nitric acid and N_2O_5 on the hexahydrate (which decomposes on heating to form Co_3O_4). Cobaltous nitrate forms with bismuth nitrate red crystals of $Co_3[Bi(NO_3)_6]_2,24H_2O$, isomorphous with similar compounds formed with zinc, manganese and nickel nitrates.

Cobaltous sulphide CoS, precipitated by ammonium sulphide, or hydrogen sulphide in presence of sodium acetate, is black. Although not precipitated by hydrogen sulphide from acid solutions, it is insoluble in dilute acids but soluble in concentrated hydrochloric acid and aqua regia. Precipitated cobalt and nickel sulphides are apparently $Co(SH)_2$ and $Ni(SH)_2$, which absorb oxygen on exposure to air, probably forming $Co\left(S\begin{smallmatrix}O\\H\end{smallmatrix}\right)_2$ and $Ni\left(S\begin{smallmatrix}O\\H\end{smallmatrix}\right)_2$, which then oxidise to sulphates (Middleton and Ward, *J.C.S.*, 1935, 1459).

Cobalt disulphide CoS_2 precipitated by yellow ammonium sulphide from a cobaltous solution, or formed by heating CoS and sulphur, has the pyrites structure (p. 853) and contains *bivalent* cobalt (De Jong and Williams, 1927).

Cobaltous sulphate $CoSO_4$, obtained anhydrous by heating a hydrate at 250°, boiling it with concentrated sulphuric acid, or heating it with ammonium sulphate, is a pale reddish or lavender-coloured powder, consisting of small rhombic crystals. All the hydrates are pink or red. The common hydrate, $CoSO_4,7H_2O$, crystallises below 44° from solutions of cobalt, oxide or carbonate in dilute sulphuric acid; it is monoclinic, isomorphous with $FeSO_4,7H_2O$ and $NiSO_4,7H_2O$, and efflorescent, m.p. 97°. Between 44° and 70° monoclinic $CoSO_4,6H_2O$ isomorphous with $ZnSO_4,6H_2O$ crystallises, and above 70° $CoSO_4,H_2O$, the solubility of which decreases with rise in temperature. Hydrates with 5 and $4H_2O$ are also known.

Red **double sulphates** $M^I_2Co(SO_4)_2,6H_2O$ (M^I=K, Rb, Cs, NH_4, Tl^I) are readily formed; they belong to the schönite group (p. 854) and are all monoclinic and isomorphous (also with corresponding compounds with bivalent Ni, Fe, Zn, Cd, Mg, etc.; Tutton, *J.C.S.*, 1905, **87**, 1123; *Phil. Trans.*, 1915, **216**, 1).

Ammonium thiocyanate gives with a cobaltous salt solution (especially in presence of acetone) a deep blue colour due to $Co(CNS)_4''$, extracted by ether or amyl alcohol; from the aqueous solution a blue salt $(NH_4)_2[Co(CNS)_4]$ can be crystallised. A mercuric salt and a thiocyanate with a cobaltous solution form a deep blue crystalline precipitate of $Co[Hg(CNS)_4]$.

Cobaltic Compounds

There is much confusion in the literature of the **higher oxides of cobalt** (cf. Kalmus, *Ind. Eng. Chem.*, 1914, **6**, 115; Howell, *J.C.S.*, 1923, **123**, 65; *Proc. Roy. Soc.*, 1923, **104**, 134). The dark brown or black powder formed on heating cobalt nitrate (sometimes described as Co_2O_3) is **cobalto-cobaltic oxide** Co_3O_4, octahedral, with a spinel structure, $Co^{II}(Co^{III}O_2)_2$, also formed by heating CoO or Co_2O_3 at 600°–700° in air. Unlike Fe_3O_4 it is non-magnetic. The black precipitate from cobalt solutions by hypochlorite, alkali and iodine, hydrogen peroxide or ammonium persulphate is hydrated **cobaltic oxide** Co_2O_3, although some **dioxide** $Co^{IV}O_2$ is formed by adding further quantities of hypochlorite.

Precipitated cobaltic hydroxide is not crystalline but gives X-ray lines of Co_2O_3, which is formed from it at 250°. Definite hydrates of Co_2O_3 with 1, 2 and $\frac{5}{3}H_2O$ are claimed from breaks in the dehydration curve. **Cobaltates**, *e.g.* crystalline $BaCo^{IV}O_3$, derived from $Co^{IV}O_2$, are described (*percobaltites*, *e.g.* Co_3O_4 or $Co(CoO_3)_2$, are derived from Co_2O_3).

Cobaltic fluoride CoF_3 is a green solid formed by the action of fluorine on $CoCl_2$ at 150°; a green hydrate $2CoF_3,7H_2O$, decomposed by water, is formed by electrolytic oxidation of a solution of CoF_2 in 40 p.c. hydrofluoric acid (Barbieri, etc., 1905–28; Ruff and Ascher, 1929). Blue **cobaltic cyanide** $Co(CN)_3$

and a red dihydrate are known (Rây, etc., 1933–4). **Cobaltic sulphide** Co_2S_3 is formed from the elements at 350°–400°. On heating precipitated CoS in H_2S at 450° Co_3S_4, with a spinel structure, is formed.

Cobaltic sulphate $Co_2(SO_4)_3,18H_2O$ is deposited in silky blue needles by electrolytic oxidation of a cooled saturated solution of $CoSO_4,7H_2O$ in 40 p.c. sulphuric acid ; it forms blue **cobaltic alums** $MCo(SO_4)_2,12H_2O$ (M = Na, K, Rb, Cs, NH_4) which (like the sulphate) are rather unstable, evolving ozonised oxygen in solution (Marshall, *J.C.S.*, 1891, **59**, 760 ; Howe and O'Neal, *J.A.C.S.*, 1898, **20**, 759). There is also a cobaltic selenate $Co_2(SeO_4)_3,18H_2O$ (Copaux, 1905). All simple cobaltic salts are powerful oxidising agents.

When hydrogen peroxide is added to a suspension of cobaltous hydroxide the filtrate is acid and gives a green colour with $KHCO_3$. It has been supposed to contain cobaltic acid H_3CoO_3, or a complex cobaltic compound $[Co(KCO_3)_2]_2O$, or a compound $CoCO_3,Co_2O_3$, or a complex cobaltic carbonate $Co[Co(CO_3)_3]$.

Complex Cobaltic Compounds

The commonest cobaltic compounds are complex, the most important being the cobaltammines, the cobaltinitrites and the cobalticyanides.

Cobaltammines.—Precipitated cobaltous hydroxide dissolves in excess of ammonia to a yellowish-brown solution which deposits cobaltous hydroxide on dilution. On exposure to air the solution absorbs oxygen, more rapidly on boiling or heating with lead dioxide, and forms a pink solution of a **cobaltammine,** containing tervalent cobalt in a complex. More than 2000 compounds of this type are known. The following are typical preparations of cobaltammines :

(i) A solution of ammonium carbonate and ammonia is added to cobalt nitrate solution and air is drawn through the violet liquid ; oxidation occurs and a blood-red solution of *tetrammine-carbonato-cobaltic nitrate* $[Co(NH_3)_4CO_3]NO_3$ is formed, which gives purple crystals (with $\frac{1}{2}H_2O$) on evaporation.

(ii) On acidifying a solution of this with hydrochloric acid, heating with excess of ammonia, and adding concentrated hydrochloric acid, *pentammine-chloro-cobaltic dichloride* $[Co(NH_3)_5Cl]Cl_2$ is formed, from the solution of which mercuric chloride precipitates rose-red needles of $[Co(NH_3)_5Cl]Cl_2,3HgCl_2$.

(iii) On heating $[Co(NH_3)_5Cl]Cl_2$ with ammonium chloride and ammonia in a pressure bottle, adding hydrochloric acid and cooling, *hexammine-cobaltic trichloride* $[Co(NH_3)_6]Cl_3$ is formed.

(iv) From a solution of $[Co(NH_3)_5Cl]Cl_2$ in ammonia, cooled in ice, slow addition of concentrated hydrochloric acid precipitates *aquo-pentammine-cobaltic trichloride* $[Co(NH_3)_5H_2O]Cl_3$.

(v) There are two isomeric (*cis* and *trans*) *dinitrito-tetrammine cobaltic chlorides* $[Co(NH_3)_4(NO_2)_2]Cl$ (p. 221). The flavo- (*cis*) compound is made from the nitrate (obtained by the action of nitric acid and sodium nitrite on $[Co(NH_3)_4CO_3]NO_3$) by precipitation with ammonium chloride and alcohol. The croceo- (*trans*) compound is made by adding ammonium chloride and sodium nitrite to cobaltous chloride, oxidising with a current of air, dissolving the precipitated crude salt in hot water acidified with acetic acid, and precipitating by solid ammonium chloride.

Cobalticyanides contain the very stable complex anion $Co(CN)_6'''$ containing 3-valent cobalt. Potassium cyanide gives with a cobalt salt solution a reddish-brown precipitate of **cobaltous cyanide** $Co(CN)_2,3H_2O$, soluble in excess to a yellow solution of **potassium cobaltocyanide** $K_4Co(CN)_6$, containing 2-valent cobalt and analogous to ferrocyanide; this is precipitated as an amethyst-coloured powder by alcohol. On adding a little acetic or hydrochloric acid to the cobaltocyanide solution and boiling in a dish for a few minutes, oxidation occurs and **potassium cobalticyanide** $K_3Co(CN)_6$, containing 3-valent cobalt and analogous to ferricyanide, is formed (Gmelin, 1827):

$$2Co(CN)_6'''' + O_2 + 2H_2O = 2Co(CN)_6''' + 2OH' + H_2O_2.$$

An equivalent amount of hydrogen peroxide is formed by autoxidation.

Potassium cobalticyanide forms stable yellow crystals isomorphous with the ferricyanide. With silver nitrate it gives a white precipitate of silver cobalticyanide $Ag_3Co(CN)_6$ and with copper sulphate a blue precipitate of cupric cobalticyanide $Cu_3[Co(CN)_6]_2$, from which by precipitation of the copper by hydrogen sulphide colourless crystalline **hydrocobalticyanic acid** $H_3Co(CN)_6$ is formed. Cobalticyanides give no reactions of cobalt or cyanide, and are not decomposed by concentrated nitric acid or hypochlorite.

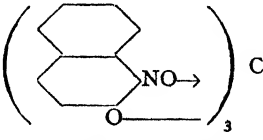
Cobaltinitrites contain the complex anion $Co(NO_2)_6'''$ containing 3-valent cobalt. Potassium nitrite gives with a cobaltous salt solution acidified with acetic acid a yellow precipitate of **potassium cobaltinitrite** $K_3Co(NO_2)_6$ (*Fischer's salt*), sparingly soluble in water:

$$Co'' + 7NO_2' + 2H' = Co(NO_2)_6''' + NO + H_2O.$$

This is formed only in acid solutions, otherwise the **cobaltonitrite** $K_2Co(NO_2)_4$, containing 2-valent cobalt, is produced. The cobaltinitrite is less stable than the cobalticyanide and is decomposed by ammonium sulphide. It is used as a yellow pigment (*Indian*, or *cobalt, yellow*) and in painting porcelain blue.

A reagent for potassium is prepared by dissolving 30 g. of cobalt nitrate and 50 g. of sodium nitrite in 150 c.c. of water and adding 10 c.c. of glacial acetic acid. The addition of silver nitrate makes it more sensitive, as the salts $K_2AgCo(NO_2)_6$ and $KAg_2Co(NO_2)_6$ are less soluble than $K_3Co(NO_2)_6$; 1 pt. of potassium in 10,000 of water may be detected (Burgess and Kamm, *J.A.C.S.*, 1912, **34**, 652; Cumbers and Coppock, *J.S.C.I.*, 1937, **56**, 405 T).

An important compound of tervalent cobalt is **cobalti-α-nitroso-β-naphthol**:



formed as a brownish-red precipitate on warming a solution of a *cobaltous* salt with a solution of α-nitroso-β-naphthol in acetic acid. Nickel is not precipitated. If the Co^{II} is converted into Co^{III} by precipitating cobaltic hydroxide by alkali and H_2O_2 and dissolving this in acetic acid, precipitation of $Co(C_{10}H_6O_2N)_3,2H_2O$ is quantitative.

Nickel

A coin of the Bactrian king Euthydemos (235 B.C.) contained 20·04 p.c. of nickel and 77·58 p.c. of copper, and alloys of copper, zinc and nickel (*paktong*) were previously used in China. The old German miners of Westphalia encountered a mineral like copper ore from which no copper could be extracted, and this was called *kupfer-nickel* (" false-copper ") by Hiärne (1694). Impure metallic nickel was obtained from it by Cronstedt in 1751, and the properties of the metal and its compounds were investigated more fully by Bergman in 1774.

Nickel and cobalt usually occur together. The chief nickel ores are the cobalt ore *smaltite* $(Ni,Co,Fe)As_2$, *chloanthite* or *white nickel ore* $NiAs_2$, *niccolite* or *kupfer-nickel* NiAs, *nickel glance* NiAsS, *millerite* NiS, the apple-green *annabergite* or *nickel bloom* $Ni_3(AsO_4)_2,8H_2O$ formed as an efflorescence on chloanthite, *garnierite* $(Ni,Mg)SiO_3,xH_2O$ found in New Caledonia, and *pentlandite* (Ni,Fe)S containing about 22 p.c. of nickel, found at Sudbury, Ontario. The magnetic pyrites of Pennsylvania contains about 5 p.c. of nickel, and nickel is obtained as a by-product in electrolytic copper refining.

The Sudbury ores, which are the most important, contain about 2·5 p.c. of nickel as pentlandite, which is separated from the accompanying chalcopyrite $CuFeS_2$ and pyrrhotite Fe_8S_9 by flotation. The fraction rich in nickel is roasted, smelted with coke, and bessemerised to give a matte containing 25–30 of Cu, 56 of Ni (sometimes with cobalt), 0·1–0·5 of Fe and 14–17 of S. This may be roasted and refined, and the mixture of copper and nickel oxides reduced by carbon in open-hearth or electric furnaces to *monel metal*, containing 67 of Ni, 28 of Cu, and 5 of Mn and Fe, and resembling nickel in colour and properties (Merica, *Chem. Met. Eng.*, 1921, **24**, 291). The copper and nickel are separated from the matte by the *Orford process*, in which it is melted with coke and saltcake (Na_2SO_4), which form sodium sulphide, in a basic-hearth furnace and poled, when two strata separate. The upper layer contains sodium and cuprous sulphides, the lower layer nickel sulphide. The top layer is bessemerised to yield copper and the lower layer is purified and roasted to nickel oxide, which is reduced by heating strongly with charcoal powder. Gold, silver and platinum metals are recovered as by-products.

Garnierite is fused with gypsum and coke and the matte blown in a converter or smelted in a reverberatory furnace with a silica flux; iron is removed and the nickel sulphide is worked as described above.

Nickel is extracted from the refined Canadian matte by the *Mond carbonyl process* (1895) at Clydach in South Wales. The roasted matte is leached with dilute sulphuric acid containing copper sulphate to remove copper as sulphate. The residue contains nickel oxide which is reduced at 300°–350° by the hydrogen contained in water gas, which is thus enriched in carbon monoxide; the ferric oxide is not reduced at this temperature. The mass is then passed at 60° down a tower with shelves, and carbon monoxide from the enriched water gas is passed through. Volatile *nickel carbonyl* $Ni(CO)_4$ is formed. The gas containing this passes through a decomposer at 150°–180°, when the carbonyl is decomposed and metallic nickel is deposited on nickel granules kept stirred,

the carbon monoxide passing back to the volatiliser : $Ni(CO)_4 \rightleftharpoons Ni + 4CO$. The metal is 99·8 p.c. pure ; it contains 0·06 p.c. of iron, 0·09 p.c. of carbon and traces of sulphur and silicon.

A little sulphur is left in the roasted matte, as this facilitates the formation of carbonyl. In casting nickel a little magnesium is added to increase the fluidity and remove gas bubbles.

Nickel is refined by electrodeposition from nickel ammonium sulphate solution saturated at 20°–25°, with a cast nickel block as anode and a thin polished sheet of pure nickel as cathode. The same process is used in nickel plating, a thin layer of copper being first deposited on iron or steel. Nickel plating is fairly easily dissolved by acids, even acetic, and soon tarnishes in town air, so that it has been replaced by chromium.

Nickel is greyish-white, s. g. 8·35 (cast)–8·9 (rolled), very hard but malleable and capable of taking a high polish. It is magnetic below 340°, when an allotropic change occurs. Finely divided nickel absorbs 17 vols. of hydrogen and is used as a catalyst in the hydrogenation of oils. Molten nickel absorbs hydrogen but liberates it by " spitting " on solidification.

Although finely divided nickel obtained by reducing the hydroxide in hydrogen at a temperature not above 300° is pyrophoric, the compact metal oxidises only slightly in air on heating and decomposes steam only slowly at a red heat : $Ni + H_2O \rightleftharpoons NiO + H_2$. It dissolves readily in dilute nitric acid and aqua regia, but is hardly attacked by dilute hydrochloric or sulphuric acid. It becomes passive in concentrated nitric acid.

Pure nickel is used for crucibles, tubes and utensils (*e.g.* for dairies). **Nickel alloys** are important.

Nickel steel contains about 3·5 p.c. of nickel. An alloy of 25 p.c. of nickel and 75 p.c. of copper is used for coinage, and one with 20 p.c. of nickel for coating rifle-bullets. *Nichrome* (60 Ni, 25 Fe and 15 Cr) melts only at a high temperature and is used for resistance heaters. *Permalloy* (66–81 Ni and the rest Fe) when heated to 950°, slowly cooled to 625° and quenched, has a very high magnetic permeability. *German silver* is the alloy 55 Cu, 20 Ni and 25 Zn and the Chinese *paktong* is similar. Alloys for resistance coils are *platinoid* (60 Cu, 24 Zn, 14 Ni and 1–2 W), *constantan* (40 Ni and 60 Cu) and *rheotan* (52 Cu, 25 Ni, 18 Zn and 5 Fe). *Illium* is an acid-resisting alloy of Ni, Cr, Fe, W, Co, Mo and Mn.

Nickel Compounds

Unlike iron and cobalt, nickel is almost uniformly bivalent although it shows valencies of 1, 3 (in Ni_2O_3) and 4 (in NiO_2 and $Ba[Ni_2O_5]$). It shows no tendency to form complexes of 3-valent Ni.

Univalent nickel is contained in the deep red solution formed on heating $K_2[Ni(CN)_4]$ solution with zinc, from which NiCN is precipitated by acid (Papasogli, 1879; Bellucci, etc., 1913–19), and in the compound $K_3\left[NO{\rightarrow}Ni\begin{matrix}S_2O_3' \\ S_2O_3''\end{matrix}\right]$ (Manchot, 1926).

Nickel hydride NiH_2 is formed as a black precipitate on passing hydrogen into an ether solution of phenyl magnesium bromide containing $NiCl_2$ (Weichselfelder and Thiede, 1926).

Nickel salts form green solutions containing the hydrated ion, probably $[Ni(H_2O)_6]^{..}$. The anhydrous compounds are often yellow and are covalent.

Nickel fluoride NiF_2 (yellowish-green, tetragonal) sublimes on heating $NiCl_2$ and NH_4F in a current of HF ; the hydrate $NiF_2,3H_2O$ (blue-green) crystallises from a solution of the hydroxide or carbonate in hydrofluoric acid. It forms an acid salt $NiF_2,5HF,6H_2O$ or $H_5[NiF_7],6H_2O$ and double salts with alkali fluorides.

Nickel chloride $NiCl_2$ sublimes in yellow hexagonal scales on heating the dehydrated compound in a stream of hydrogen chloride. The hydrate $NiCl_2,6H_2O$ deposits in green deliquescent monoclinic prisms from a solution of the metal in aqua regia or the oxide in hydrochloric acid. At 70° it forms $NiCl_2,4H_2O$ and at a higher temperature yellow $NiCl_2$. Hydrates with 2 and $1H_2O$ are known, also compounds of $NiCl_2$ with 6, 2 and $1NH_3$ and ND_3 (Hart and Partington, *J.C.S.*, 1943, 104). Double salts are $NH_4NiCl_3,6H_2O$ (monoclinic), Rb_2NiCl_4 and Cs_2NiCl_4.

Nickel bromide $NiBr_2$ (yellow) and $NiBr_2.3H_2O$ (green) and **nickel iodide** NiI_2 (black) and $NiI_2,6H_2O$ (bluish-green) are formed similarly to the chloride and are deliquescent.

Nickel monoxide NiO is formed as a green crystalline powder by strongly heating the hydroxide, carbonate or nitrate (Prasad and Tendulkar, *J.C.S.*, 1931, 1403). It forms octahedral crystals. Compounds of NiO with alumina ($NiAl_2O_4$, blue) and stannic and zinc oxides are formed at high temperatures (Hedvall, 1918).

Nickel hydroxide $Ni(OH)_2$, which is a definite compound (Hüttig and Peter, 1930), is formed as an apple-green precipitate by alkali hydroxide, insoluble in excess but somewhat soluble in ammonia to a blue solution (from which it separates as a green hexagonal-crystalline powder on boiling) and in ammonium salts.

Nickel sesquioxide or **nickelic oxide** Ni_2O_3 is black and contains tervalent nickel. It is formed on moderate heating of nickel nitrate and is fairly stable : it loses oxygen above 340° but is stable in oxygen to 450° (Foote and Smith, *J.A.C.S.*, 1908, **20**, 1344). It liberates chlorine from hydrochloric acid. A black **nickelic hydroxide** Ni_2O_3,H_2O or NiO(OH) is precipitated on passing chlorine into a suspension of $Ni(OH)_2$, or warming a nickel salt solution with alkali hypochlorite, and exists in two forms : Ni_2O_3,H_2O or O=Ni—OH and $Ni_2O_3,2H_2O$ or $(HO)_2$=Ni—O—Ni=$(OH)_2$ (Cairns and Ott, *J.A.C.S.*, 1933, **55**, 525, 534 ; Hüttig and Peter, 1930).

According to Bellucci and Clavari (1905–7) this is the hydrated **dioxide** NiO_2 of 4-valent nickel, which rapidly loses oxygen ; the precipitate contains both Ni_2O_3 and NiO_2, the proportion of NiO_2 increasing with the amount of hypochlorite (Howell, *J.C.S.*, 1923, **123**, 669, 1772). A compound $BaO,2NiO_2$ or $Ba[Ni_2O_5]$ is said to be formed by heating $BaCO_3$ and Ni_2O_3 in the electric furnace

(Dufau, 1896), and compounds of NiO_4 and Ni_2O_5 have been reported (Hollard, 1903; Goralevich, 1930).

A green hydrated **nickel peroxide**  , aq., which forms hydrogen peroxide with acids, is precipitated by cooled alcoholic potash from an alcoholic solution of $NiCl_2$ and H_2O_2 cooled in ice and salt.

Nickel carbonate $NiCO_3,6H_2O$ is obtained as a green precipitate on adding dilute potassium bicarbonate solution to a large excess of nickel chloride solution. With a large excess of potassium bicarbonate a double salt $KHNi(CO_3)_2,4H_2O$ is precipitated (Nanty, 1913). The precipitate with normal alkali carbonate contains nickel hydroxide. Anhydrous $NiCO_3$ is formed by the action of carbon dioxide and water on nickel under pressure.

Nickel nitrate $Ni(NO_3)_2,3H_2O$ deposits in green monoclinic deliquescent crystals from a solution of nickel in dilute nitric acid. Hydrates with 9, 4, 3 (?) and $2H_2O$ are described, and there are double nitrates, *e.g.* $3Ni(NO_3)_2$, $2Bi(NO_3)_3,24H_2O$. Since the salt decomposes on heating, anhydrous $Ni(NO_3)_2$ must be prepared in the same way as the cobalt salt (p. 867).

No compounds analogous to cobaltinitrites (p. 870) are formed; the compound of bivalent nickel $K_4[Ni^{II}(NO_2)_6]$ is soluble, but in presence of a calcium salt sparingly soluble yellow $K_2Ca[Ni(NO_2)_6]$, similar in appearance to the cobaltinitrite, is precipitated.

The bright red **potassium nickelocyanide** $K_2[Ni(CN)_4],H_2O$ is formed by addition of excess of potassium cyanide to a nickel salt solution, when the green $Ni(CN)_2$ precipitate redissolves, and crystallising. It shows no tendency to oxidise to a tervalent nickel compound in air, is easily decomposed by acids, and hypochlorite precipitates black hydrated Ni_2O_3. The behaviour of nickel is thus quite different from that of cobalt, which more closely resembles iron.

Nickel sulphide NiS occurs as bronze-yellow *millerite*. There are two forms, hexagonal and rhombohedral. The black precipitate formed on adding ammonia and ammonium sulphide to a nickel salt solution may be $Ni(SH)_2$ (see p. 867); it dissolves slightly in excess of ammonium polysulphide to a dark brown solution, from which it is precipitated by boiling, exposure to air, or addition of acid. The moist precipitate easily oxidises on exposure to air. A dense black sulphide, not easily oxidised, is precipitated by boiling a nickel salt solution with sodium thiosulphate. Nickel sulphide is insoluble in dilute acids but dissolves slowly in concentrated hydrochloric acid, and readily in nitric acid and aqua regia.

Although nickel sulphide is not precipitated by hydrogen sulphide in presence of dilute hydrochloric acid, the precipitate obtained in alkaline solution is insoluble in dilute acid. It is supposed that three different forms of the sulphide are precipitated under different conditions (Thiel and Gessner, 1914; Dunn and Rideal, *J.C.S.*, 1923, **123**, 1242).

Nickel sulphate $NiSO_4,7H_2O$ separates in green rhombic prisms isomorphous with Epsom salt from a solution of the oxide or basic carbonate in dilute

sulphuric acid on evaporation at room temperature. Prolonged exposure to air gives a blue tetrahydrate; above 54° in contact with saturated solution a bright green monoclinic hexahydrate is formed. Heating at 118° gives the dihydrate, and above 280° yellow anhydrous $NiSO_4$ (which, unlike $CuSO_4$, does not react with HCl). Many double salts are known, *e.g.* bluish-green monoclinic $(NH_4)_2Ni(SO_4)_2,6H_2O$, readily soluble in water but almost insoluble in acidified ammonium sulphate solution.

A characteristic reaction of nickel is the formation of a bright red precipitate (with 0·01 mg. Ni) with dimethylglyoxime (p. 216); α-diphenylglyoxime is even more sensitive (1 of Ni in 10^6).

The Metal Carbonyls

The metal **carbonyls** proper are covalent compounds of metals with carbon monoxide (p. 482). They form two main groups:

(*A*) **Volatile,** unimolecular, very soluble in non-polar solvents:

$Cr(CO)_6$ $Mo(CO)_6$ $W(CO)_6$ white crystals, rather stable and inert	$Fe(CO)_5$ yellow liquid, b.p. 102·5°, m.p. −20°	$Ni(CO)_4$ colourless liquid b.p. 43·2°, m.p. −25°
	$Ru(CO)_5$ colourless liquid, m.p. −22°	

(*B*) **Non-volatile,** solid, polymerised, sparingly soluble in non-polar solvents:

$[Re(CO)_5]_2$	$Fe_2(CO)_9$ yellow, decomp. at 100°	$[Fe(CO)_4]_3$ dark green, decomp. at 140°	$[Fe(CO)_3]_x$ red
	$Ru_2(CO)_9$ orange-yellow	$[Co(CO)_4]_2$ orange, m.p. 51°, decomp. 52°	$[Co(CO)_3]_4$ black, decomp. at 60°
		$[Ru(CO)_4]_x$ green	$[Ir(CO)_3]_x$ yellow
		$[Ir(CO)_4]_x$ greenish-yellow	

General methods of preparation (Mond, *J.S.C.I.*, 1930, **49**, 271, 283, 287 T.; Blanchard, *Chem. Reviews*, 1937, **21**, 3; 1940, **26**, 409; Hieber, *Z. Elektrochem.*, 1937, **43**, 390; *Ann. Rep. C.S.*, 1934, **31**, 99; 1941, **38**, 71) are:

(i) The action of carbon monoxide on the finely divided metal at moderate temperature, in entire absence of oxygen. Except with Ni and Fe the reaction is carried out under pressure.

(ii) The Grignard reaction between the anhydrous metal chloride and phenyl magnesium bromide in dry ether, followed by passing in carbon monoxide gas and then hydrolysis. (This is the only method for chromium carbonyl.)

The most important carbonyls are nickel carbonyl $Ni(CO)_4$ (discovered by Mond, Langer and Quincke in 1888) and iron pentacarbonyl $Fe(CO)_5$ (discovered by Berthelot, and by Mond and Quincke, in 1891).

Nickel carbonyl $Ni(CO)_4$ is a colourless strongly refracting liquid, with the normal molecular weight as vapour or in solution. It is formed by passing carbon monoxide over finely divided (reduced) nickel at 30°. At higher pressure a higher temperature can be used without decomposition, *e.g.* at 100 atm. decomposition does not occur even at 250°. The pure vapour explodes at 60°: $Ni(CO)_4 = Ni + 2CO_2 + 2C$, but when diluted with carbon monoxide it decomposes reversibly on heating: $Ni(CO)_4 \rightleftharpoons Ni + 4CO$, and in a glass tube nickel deposits as a mirror. A mixture of the vapour and air is explosive and poisonous. Nickel carbonyl is not decomposed by water free from air, or by dilute acids or alkalis. Halogens decompose it rapidly, forming nickel halide and carbon monoxide; dry hydrogen chloride and bromide react only very slowly, but dry hydrogen iodide reacts: $Ni(CO)_4 + 2HI = NiI_2 + H_2 + 4CO$.

Iron pentacarbonyl $Fe(CO)_5$ is formed by passing carbon monoxide over finely divided iron at 120°. It is prepared industrially under pressure and is formed in traces when water-gas is passed through iron pipes or coal gas is stored under pressure in iron cylinders, and such gas deposits ferric oxide on incandescent mantles of gas burners. Iron pentacarbonyl is a pale yellow viscous liquid. The vapour density is normal at 129° and the freezing point of a solution in benzene corresponds with the formula $Fe(CO)_5$. The vapour decomposes on passing through a tube heated at 180°, depositing an iron mirror.

Iron pentacarbonyl is decomposed by air, moisture and acids: $Fe(CO)_5 + H_2SO_4 = FeSO_4 + H_2 + 5CO$. On exposure to light it forms orange crystals of $Fe_2(CO)_9$, the reaction being reversed in the dark: $2Fe(CO)_5 \rightleftharpoons Fe_2(CO)_9 + CO$. The crystals decompose on heating: $Fe_2(CO)_9 = Fe(CO)_5 + Fe + 4CO$. A solution of $Fe(CO)_5$ in toluene becomes intensely green on heating at 50° and deposits green crystals of $[Fe(CO)_4]_3$.

At low temperatures $Fe(CO)_5$ and halogens form $Fe(CO)_5X_2$, and by the action of pyridine and mercury $Fe(CO)_5I_2$ gives $Fe(CO)_2I_2py_2$ and $Fe(CO)_3I_2Hg_2$. With barium hydroxide solution followed by acidification $Fe(CO)_5$ forms **iron carbonyl hydride** $H_2Fe(CO)_4$, which can be distilled off in vacuum and is acidic and a strong reducing agent: $Fe(CO)_5 + Ba(OH)_2 = H_2Fe(CO)_4 + BaCO_3$. By the action of nitric oxide on a solution of $[Fe(CO)_4]_3$ in $Fe(CO)_5$ **iron nitrosocarbonyl** $Fe(CO)_2(NO)_2$ is formed, 2CO being replaced by 2NO. This forms red crystals. It reacts with iodine in benzene to give $Fe(NO)_2I$, containing univalent iron. $H_2Ru(CO)_4$ and $HIr(CO)_4$ are reported.

Unlike nickel and iron, cobalt does not form a carbonyl at ordinary pressure and no volatile cobalt carbonyl is known. Solid $[Co(CO)_4]_2$ is formed at 200° and 200 atm. By the action of barium hydroxide and acidification this forms acidic **cobalt carbonyl hydride** $HCo(CO)_4$, which can be distilled off in vacuum: $3[Co(CO)_4]_2 + 2Ba(OH)_2 = 4HCo(CO)_4 + 2BaCO_3 + \frac{1}{2}[Co(CO)_3]_4$. Nitric oxide reacts with $[Co(CO)_4]_2$ to give the **nitrosocarbonyl**: $[Co(CO)_4]_2 + 2NO = 2Co(CO)_3(NO) + 2CO$.

Many **carbonyl halides** are known, *e.g.* CO in $Fe(CO)_5$ can be replaced in stages by halogen to $Fe(CO)_2X$; the volatile platinous compounds $Pt(CO)_2X_2$ and $Pt_2(CO)_2X_4$ have long been known and all the metals of the platinum group, also copper and gold, form such compounds.

The *structure of the metal carbonyls* has been studied by Raman spectra, X-rays and electron diffraction. The CO is linked covalently to the metal by the unshared pair of electrons on the carbon:

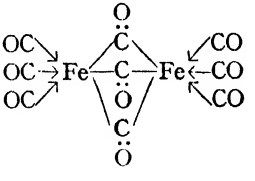
$$:C:\overset{\times}{\underset{\times}{\times}}O\overset{\times}{\times} \qquad \leftarrow C \rightleftharpoons O$$

e.g. $\begin{matrix} OC\rightarrow & & \leftarrow CO \\ OC\rightarrow & Ni & \leftarrow CO \end{matrix}$. Langmuir (1921) pointed out an interesting relation between the *effective atomic number* (E.A.N.) = no. of electrons of metal + electrons donated by CO, and the electron shells of the inert gas at the end of the period in which the metal occurs :

	E.A.N.	
$Ni(CO)_4$	$28+8=36$	Kr 36
$Fe(CO)_5$	$26+10=36$	Kr 36
$Ru(CO)_5$	$44+10=54$	Xe 54
$W(CO)_6$	$74+12=86$	Rn 86

Since cobalt has 27 electrons it cannot form a carbonyl with an inert gas structure, but can form a nitrosocarbonyl $Co(CO)_3(NO)$ by the donation of the odd electron of the NO to the metal to form 28 electrons, as in nickel, the residue of the NO and three CO molecules then forming coordinate links with four pairs of electrons. $Co(CO)_3(NO)$ is thus analogous to $Ni(CO)_4$ and the two molecules have tetrahedral structures and very similar properties. $Fe(CO)_5$ has the structure of a trigonal bipyramid.

The structures of the higher carbonyls are mostly unknown but $Fe_2(CO)_9$ is shown by X-ray analysis to have 6 CO molecules linked by coordination and 3 CO groups joining the iron atoms by ordinary carbonyl linkages (Powell and Evans, *J.C.S.*, 1939, 286) :



The carbonyl hydrides $H_2Fe(CO)_4$ and $HCo(CO)_4$ are tetrahedral and are supposed to be $Fe(CO)_2(COH)_2$ and $Co(CO)_3(COH)$, with the structure M : C : : : O : H for the COH linkage, the hydrogen being easily lost (Ewens and Lister, *T. Faraday Soc.*, 1939, **35**, 68).

CHAPTER XXXI

PLATINUM METALS AND INERT GASES

The Platinum Metals

THE two triads Ru, Rh, Pd and Os, Ir, Pt, usually called the *platinum metals* since they all occur in native platinum, form many compounds in which, as transitional elements, they show several valencies. The common palladium compounds are PdX_2, of bivalent palladium ; platinum forms PtX_2 and PtX_4 ; ruthenium and rhodium are most stable in tervalent compounds RuX_3 and RhX_3. Ruthenium and osmium are notable in forming volatile tetroxides RuO_4 and OsO_4, and osmium an octofluoride OsF_8, in which the metals have the maximum valency of 8.

A list of some typical compounds showing the various valencies of the platinum metals is given below. Ruthenium is notable in showing all valencies from 1 to 8.

1	2	3	4	5	6	7	8
OC ›RuBr	$RuCl_2$ (?)	$RuCl_3$	$RuCl_4$	RuF_5	K_2RuO_4	$KRuO_4$	RuO_4
	$K_4Ru(CN)_6,3H_2O$	$HRuCl_4,2H_2O$	$K_2Ru(OH)Cl_5$		$H_2RuO_2Cl_4,3H_2O$		
RhCl	$Ru(dip)_2Cl_2,6H_2O$	$K_2Ru(NO)Cl_5$	RuO_2	IrF_5	RhO_3		OsF_8
RhBr	RuS_2	$K_2Ru(NO_2)_5$					OsO_4
			RhF_4 (?)		IrF_6		OsS_4
PdCl	$RhCl_2$	$RhCl_3$	RhO_2,xH_2O		IrO_3		$KOsO_3N$
Pd_2S	RhO	Rh_2O_3					
$K_2Pd(CN)_2$		$Rh_2(SO_4)_3$	PdO_2		OsF_6		
$KPd(CN)_2$	$PdCl_2(Br_2,I_2)$	$K_3Rh(NO_2)_6$	K_2PdCl_6		K_2OsO_4		
	PdO	$K_3Rh(CN)_6$			$K_2OsO_2(CN)_4$		
——	$Pd(NO_3)_2$	$K_3Rh(SCN)_6$	OsF_4		$Na_2OsO_2(NO_2)_4$		
	PdS_2	$Rh(NH_3)_6Cl_3$, etc	OsO_2				
			K_2OsCl_6		PtO_3		
IrCl	$OsCl_2$	PdF_3	$Os(OH)Cl_3$				
	$OsSO_3$	Pd_2O_3					
PtCl (?)	OsS_2		IrF_4				
		$OsCl_3$	$IrCl_4$				
	$IrCl_2$	$K_2Os(NO_2)_5$	IrO_2				
	$PtCl_2(Br_2,I_2)$						
	PtO	$IrCl_3$	$PtCl_4$				
	PtS_2	$Ir(OH)_3$	PtO_2				
	K_2PtCl_4, etc.	Ir_2S_3	H_2PtCl_6, etc.				
		$Ir_2(SO_4)_3$ and alums					
		$K_3Ir(CN)_6$					
		$PtCl_3(I_2)$					
		$Pt(CN)_3$					
		Pt_2O_3					

The lattice structures of the crystals are :

Pd, Pt, Ir, Rh face-centred cubic ; Ru, Os close-packed hexagonal ; RuO_2, IrO_2, OsO_2 tetragonal (SnO_2), PdO tetragonal (PbO), Rh_2O_3 hexagonal (Fe_2O_3) ;

PtS_2 is hexagonal (CdI_2) ; RuS_2, $RuSe_2$, $RuTe_2$, RhS_2, $PtAs_2$, OsS_2, $OsSe_2$ and $OsTe_2$ are cubic (pyrites) and hence probably contain bivalent metal ;

$PtBr_2$, cubic face-centred ;

K_2PtCl_6, K_2OsCl_6 cubic ;

K_2PdCl_4, K_2PtCl_4, $KOsNO_3$, $MgPt(CN)_4,7H_2O$ tetragonal ; $K_2OsO_2Cl_4$ tetragonal face-centred ;

$K_3Ir(CN)_6$, $[Rh(NH_3)_5Cl]Cl_2$ rhombic ; $K_2Pt(SCN)_6$ hexagonal.

Although the platinum metals are often regarded as " noble " metals like gold, this applies strictly only to platinum itself, since the other metals, especially if finely divided, all oxidise more or less on heating in air or oxygen, notably ruthenium and osmium (which burn in oxygen on heating), forming RuO_2 and RuO_4, Rh_2O_3, PdO, OsO_4, and a mixture of Ir oxides. Sometimes the oxidation is superficial and at higher temperatures the metal is again formed.

The hieroglyphs on an Egyptian box of the 7th cent. B.C. consist of an alloy of platinum, iridium, and gold. Scaliger (1557) says there was found in Mexican mines a metal " which no fire or art of the Spaniards can bring to liquefaction." Specimens of platinum (called by the natives *platina de pinto*) brought to Europe from Columbia in 1741 by Charles Wood were examined by William Brownrigg in 1750, Lewis in 1754, Marggraf in 1757, and Bergman in 1777. Platinum foil and wire were first made in 1772 by Count von Sickingen, an ambassador in Paris, and in 1806 they were sold in London for chemical purposes at 16*s*. an ounce.

The platinum metal deposits are in Russia (discovered in 1823), California, Columbia, Canada, Borneo and Australia (especially New South Wales). Platinum metals in the nickel ores of Sudbury, Ontario (p. 871), are extracted on an important scale as by-products of the Mond nickel process (Macdonald, *J.S.C.I.*, 1931, **50**, 1031 R.). Platinum occurs in several hard rocks in South Africa, but the native metal is usually obtained by washing alluvial sands and gravels. The concentrates are metallic grains, in a Russian specimen with the following composition:

Pt	Ir	Rh	Pd	Au	Cu	Fe	Osmiridium	Sand
76·4	4·3	0·3	1·4	0·4	4·1	11·7	0·5	1·4

Osmiridium is a native alloy of osmium and iridium with small amounts of other metals:

Osmium	Iridium	Platinum	Rhodium	Ruthenium
27·2	55·2	10·1	1·5	5·9

It is very hard and is used for the tips of gold pens.

The gold is extracted by amalgamation and the platinum metals are digested with aqua regia, when osmiridium remains undissolved. In one process the solution is evaporated to dryness and the residue heated at 125°. Palladium and rhodium form insoluble chlorides $PdCl_2$ and $RhCl_3$. On treating with water, platinic chloride $PtCl_4$ and a little iridium chloride $IrCl_4$ dissolve. The solution is acidified with hydrochloric acid and the chloroplatinic acid H_2PtCl_6 precipitated with ammonium chloride as the sparingly soluble $(NH_4)_2PtCl_6$. The iridium remains in solution. On heating, the ammonium chloroplatinate decomposes, leaving spongy platinum, which when heated to redness and hammered welds into a coherent metal. The metal is generally fused in the oxyhydrogen flame or in an electric furnace. The process used with the Sudbury residues at Acton, London, recovers all the platinum metals.

On adding potassium or mercuric cyanide to the solution of crude platinum in aqua regia pale yellow **palladous cyanide** $Pd(CN)_2$ is precipitated and on heating

to redness this gives metallic **palladium** (Wollaston, 1803). **Osmium** and **iridium** (Tennant, 1804) are contained in *osmiridium*. When this is fused with sodium chloride in a current of chlorine **osmic chloride** $OsCl_4$ volatilises. The solution of the residue in hydrochloric acid is treated with hydrogen, when platinum and **ruthenium** (Claus, 1845) are deposited. On passing more hydrogen into the decanted green liquid, **iridium** is precipitated. On fusing the precipitate of platinum and ruthenium with potassium nitrate and hydroxide **potassium ruthenate** K_2RuO_4 is formed. The orange-yellow solution of this when distilled in a current of chlorine gives the volatile **ruthenium tetroxide** RuO_4. **Rhodium** is contained in the aqua regia solution of crude platinum after precipitation with ammonium chloride. Ammonia is added, the solution evaporated, and the residue ignited, when metallic rhodium is formed (Wollaston, 1804).

Ruthenium

Ruthenium is white, hard and of high m.p. On heating in air it oxidises to a brown film of RuO_2 and at higher temperature to the volatile RuO_4. It is hardly attacked by acids, only slowly by aqua regia. Ruthenium shows all valencies from 1 to 8, compounds of Ru^{III} being most stable.

(1) The white solid carbonyl compound $OC{\rightarrow}RuBr$ is formed by heating $RuBr_3$ in CO at 350 atm.

(2) A blue solution of $RuCl_2$ is formed by reducing an acid solution of $RuCl_3$ with sodium amalgam, and the impure solid by the action of chlorine and CO on excess of the metal. $K_4[Ru^{II}(CN)_6],3H_2O$, made by fusing $RuCl_3$ with excess of KCN, colourless crystals isomorphous with the ferrocyanide and giving a rich purple precipitate with ferric chloride, and the free acid, are known. $[Ru(dip)_3]Cl_2,6H_2O$ (dip = 2,2′-dipyridyl) and other salts have been resolved into optical isomers. RuS_2 is formed by heating $RuCl_3$ and sulphur in H_2S : it occurs as the mineral *laurite*.

(3) $RuCl_3$ is formed in black crystals (hexagonal layer lattice) by passing chlorine with a trace of CO over heated Ru and by evaporating RuO_4 with hydrochloric acid. With hydrochloric acid it gives $H[Ru^{III}Cl_4(H_2O)_2]$ in two forms : red *cis* and green *trans*, and *cis*-salts are known. The brown supposed M_2RuCl_5, giving a red solution, is really $M_2[Ru^{IV}Cl_5OH]$. The violet-black nitrosochloride $K_2[Ru(NO)Cl_5]$, giving a violet solution, is formed by the action of nitric acid on $K_2Ru^{IV}Cl_6$, and the NO can be replaced by CO. ***Ruthenium red***, formed from $RuCl_3$ and aqueous ammonia (Joly, 1892), has the composition $[RuCl(OH)(NH_3)_4]Cl,H_2O$ but is probably a polynuclear compound (Gleu and Breuel, 1938). $K_2[Ru(NO_2)_5]$ is orange-red.

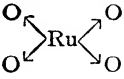
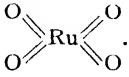
(4) $RuCl_4,5H_2O$ is obtained in reddish-brown crystals by evaporating a solution of RuO_4 in hydrochloric acid in a stream of chlorine and forms complex salts $M_2[RuCl_6]$. The deep blue RuO_2 sublimes on heating Ru powder in oxygen at 1000°. The red amorphous disulphate $Ru(SO_4)_2$ is formed by evaporating RuO_4 with sulphuric acid.

(5) Dark green RuF_5, m.p. 101°, is formed from the elements at 280°.

(6) Alkali *ruthenates* $M_2^{I}Ru^{VI}O_4$, red with a green lustre, are formed by fusing Ru or RuO_2 with alkali hydroxide and nitrate. They give deep orange oxidising solutions ; Mg, Ca, Sr, Ba and Ag salts are known. The oxide RuO_3 is not known. Purple salts $M_2^{I}[RuO_3Cl_4]$ are formed from RuO_4, RbCl or CsCl, and a little cold hydrochloric acid : $RuO_4 + 4HCl + 2MCl = M_2RuO_3Cl_4 + Cl_2 + 2H_2O$. and the free acid from RuO_4, HCl and chlorine. On boiling with concentrated

hydrochloric acid the salts form $M_2Ru^{IV}Cl_6$ and chlorine : they are decomposed by water to black solutions.

(7) Black crystalline alkali *perruthenates* $M^IRu^{VII}O_4$, giving green solutions, are formed by passing chlorine into ruthenate solutions : $2Ru^{VI}O_4'' + Cl_2 = 2Ru^{VII}O_4' + 2Cl'$, and decompose on heating : $2KRuO_4 = K_2RuO_4 + RuO_2 + O_2$ (cf. $KMnO_4$). $KRuO_4$ is tetragonal (like $KReO_4$) and not isomorphous with $KMnO_4$ (rhombic).

(8) RuO_4 in brown or yellow rhombic crystals, m.p. 25·5°, is formed by heating Ru in excess of oxygen and volatilises on passing chlorine through alkali ruthenate solution. It sublimes in vacuum but decomposes explosively into RuO_2 and O_2 at 106° ; it explodes violently in contact with alcohol. RuO_4 has a smell of ozone but does not attack the eyes so powerfully as OsO_4 and is not so poisonous. The formula is often written  but may be  .

Osmium

Osmium is bluish-grey, very hard and infusible (m.p. 2750°) : it was used before tungsten for lamp filaments. When finely divided it burns spontaneously in air and the compact metal burns in oxygen at 400°, forming OsO_4 vapour. It is attacked by chlorine, and burns in sulphur vapour on heating, is oxidised by concentrated nitric acid and dissolves in aqua regia. On fusing with alkali hydroxide exposed to air it forms an osmate, *e.g.* K_2OsO_4. The metal is formed by heating $(NH_4)_2OsCl_6$ in absence of air.

Osmium shows the valencies 2, 3, 4, 6 and 8, the last three being the commonest.

(2) Black insoluble $OsCl_2$ is formed by heating $OsCl_3$ at 500°. No $M_2^IOsCl_4$ salts are known. The sulphite $OsSO_3$ is formed in blue solution by reducing OsO_4 solution with SO_2 : on evaporation it forms a black insoluble powder. The complex cyanide $K_4[Os^{II}(CN)_6],3H_2O$ is yellow and isomorphous with the Fe^{II} and Ru^{II} salts ; it gives a blue precipitate with ferric salts. The free acid $H_4Os(CN)_6$ is known. OsS_2 has a pyrites lattice.

(3) The red or black insoluble $OsCl_3$ is formed from Os and chlorine at 1050° : it forms K_3OsCl_6, etc. The compounds $K_2[Os(NO_2)_5]$, $K_2[Os(NO)X_5]$ (X = Cl, Br, I) are isomorphous with the Ru^{III} compounds.

(4) OsF_4 (forming K_2OsF_6), $OsCl_4$ (red), $OsBr_4$ and OsI_4 (violet-black) are soluble, and the compounds $M_2^I[OsX_6]$ (X = Cl, Br, I) are formed from OsO_4, HX and MX, and $(NH_4)_2OsCl_6$ by precipitating $OsCl_4$ solution with NH_4Cl. Evaporation of OsO_4 solution in hydrogen chloride gas gives $Os(OH)Cl_3$, dissolving in hydrochloric acid to form (probably) $H_2[Os(OH)Cl_5]$ giving salts $K_2[Os(OH)Cl_5]$, etc.

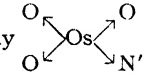
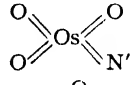
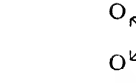
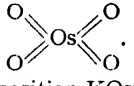
Black OsO_2 is formed by heating the very finely divided metal in OsO_4 vapour and nitrogen at 650°, and the black hydrate $OsO_2,2H_2O$ (which may explode on heating) by reducing OsO_4 solution with organic matter, or K_2OsO_4 solution with alcohol.

(6) Light green crystals of OsF_6 are formed (with OsF_8) by the action of F_2 on finely divided osmium at 250°. OsO_3 is apparently not known but deep red *osmates*, $M_2^IOsO_4$, *e.g.* $K_2OsO_4,2H_2O$, are formed by reducing solutions of OsO_4 in alkali with alcohol. The *osmyl salts*, *e.g.* $K_2[OsO_2Cl_4]$ and $Na_2[OsO_2(NO_2)_4]$ contain the radical OsO_2, and the *osmyloxy salts*, *e.g.* $(NH_4)_2[OsO_3Cl_2]$ and $K_2[OsO_3(NO_2)_2],3H_2O$ contain the radical OsO_3.

(7) A supposed $Os(OH)O_3Br'$ ion is doubtful.

(8) Yellow OsF_8, m.p. 34·5°, b.p. 47·5°, is formed from the elements. The volatile *osmium tetroxide* (often called " osmic acid "), m.p. 40·6°, b.p. 131·2°, is the most important osmium compound. It sublimes in greenish-yellow monoclinic crystals on burning finely divided osmium in oxygen. It has a very irritating smell resembling that of bromine (hence the name of the element, from Greek *osme*, a smell) and attacks the eyes powerfully (it may cause blindness), even in the vapour from the 1 p.c. solution, which is used in microscopy for staining fat globules, being reduced to black hydrated OsO_2. It is not a true acid anhydride but forms brown additive compounds $OsO_4,2KOH$, $OsO_4,RbOH$, $OsO_4,CsOH$ and $2OsO_4,CsOH$. With potassium hydroxide and ammonia solution it forms yellow tetragonal crystals of *potassium osmiamate* :

$$OsO_4 + KOH + NH_3 = KOsO_3N + 2H_2O.$$

The OsO_3N' ion is nearly tetrahedral and the structure is probably  or  (Jaeger and Zanstra, 1932), that of osmium tetroxide being  or  . On heating at 440° the osmiamate forms a blue residue of composition $KOsO_3$.

Rhodium

Rhodium is hard, white and brilliant, and has been used in plating silver to prevent tarnishing, *e.g.* for searchlight reflectors. The 10 p.c. alloy with platinum is used with pure platinum in thermocouples. Rhodium oxidises superficially on heating in air to a film of Rh_2O_3.

Rhodium is precipitated from the crude platinum solution (after precipitation of $(NH_4)_2PtCl_6$ by NH_4Cl) either by adding excess of ammonia and evaporating, when the bright yellow $[Rh^{III}(NH_3)_5Cl]Cl_2$ is formed, or by precipitating as white $K_3Rh^{III}(NO_2)_6$ (Wichers, *J.A.C.S.*, 1935, **57**, 2565). On heating $[Rh(NH_3)_5Cl]Cl_2$ in hydrogen, Rh is formed ; $K_3Rh(NO_2)_6$ is dissolved in hydrochloric acid, NH_4Cl added, $(NH_4)_3RhCl_6$ precipitated with alcohol, and ignited to Rh.

Rhodium is insoluble in nitric acid and aqua regia but is attacked by fused alkali and nitrate, or sodium peroxide. It is attacked by chlorine above 250° most easily of all platinum metals, forming $RhCl_3$. *Rhodium black*, formed by reduction, is a powerful catalyst : it decomposes formic acid : $H{\cdot}COOH = H_2 + CO_2$. *Colloidal rhodium* is used medicinally.

Rhodium shows the valencies 1, 2, 3, 4 and 6.

(1) Copper-red RhCl is formed by heating $RhCl_2$ at 948°–968°, and grey Rh_2O by heating Rh_2O_3 above 900° . they are insoluble in acids.

(2) Copper-red $RhCl_2$ is formed by heating $RhCl_3$ in chlorine at 948°, and dark grey RhO by heating Rh_2O_3 ; they are insoluble in acids.

(3) The Rh^{III} compounds, usually rose-red (Greek *rhodon*, a rose), are the most stable. Red RhF_3 is formed by heating $RhCl_3$ in fluorine. Red $RhCl_3$, insoluble in water, is formed by heating Rh or a Rh-tin alloy in chlorine : it forms dark red salts, *e.g.* $Na_3[Rh^{III}Cl_6],12H_2O$. $RhCl_3$ and hydrochloric acid give $H[Rh^{III}Cl_4(H_2O)_2]$ in two forms, a red *cis* and a green *trans*. $K_2[Rh^{III}Cl_5(H_2O)]$

is stable and the H_2O is removed only with difficulty. The blue-black Rh_2O_3 is formed by heating the metal or $RhCl_3$ in oxygen at 600°–1000°; the citron-yellow $Rh_2O_3,5H_2O$, precipitated from Rh^{III} solutions by alkali, is easily soluble in acids. The sulphate $Rh_2(SO_4)_3,15H_2O$ forms yellow alums with K, NH_4, Rb, Cs, Tl^I, isomorphous with common alum, *e.g.* $CsRh(SO_4)_2,12H_2O$. The stable salts $M_3[Rh(SCN)_6]$ are isomorphous with the Fe^{III}, Co^{III} and Ir^{III} salts and the free acid $H_3Rh(SCN)_6$ is known. Stable ammines are formed from $[Rh(NH_3)_6]Cl_3$ to $[RhCl_3(NH_3)_3]$.

(4) Red RhF_4 (which may be RhF_5) is formed from the elements. Green $RhO_2,2H_2O$ is formed by electrolysis of Na_3RhCl_6 in excess of alkali; on drying it forms Rh_2O_3 and it evolves chlorine with hydrochloric acid, forming $RhCl_3$.

(6) $RhO_3.xH_2O$ is formed as a deep blue precipitate on adding alkali to the deep purple solution formed by the electrolytic oxidation of a solution of $Rh(ClO_4)_3$ in perchloric acid. It evolves chlorine with hydrochloric acid and dissolves in excess of alkali to a deep blue solution (*Claus's blue*, 1860), probably containing a *rhodate* K_2RhO_4.

The *sulphides* Rh_9S_8, Rh_3S_4, Rh_2S_3, RhS_2 and Rh_2S_5 are described.

Iridium

Iridium is white, hard and brittle, with a very high m.p. (2440°). It oxidises in air appreciably above 800° to volatile Ir_2O_3 but is insoluble in aqua regia and attacked by fluorine only at a red heat.

Iridium is very hard and is used for the tips of gold pens. Iridium crucibles resist the action of carbon, phosphorus, and aqua regia. The standard metre of Paris was constructed by Johnson and Matthey in London from an alloy of 9 parts of platinum and 1 part of iridium. The same alloy is used, with pure platinum, in thermocouples. Since iridium volatilises above 1000°, an alloy of platinum and rhodium is used at higher temperatures.

Iridium shows valencies of 1, 2, 3, 4, 5 and 6, the Ir^{III} and Ir^{VI} compounds being most stable.

(1) IrCl, copper-red and insoluble, is formed on heating $IrCl_2$ in chlorine at 790°.

(2) $IrCl_2$, brown and insoluble, is formed by heating $IrCl_3$ in chlorine at 763°–773°. IrS is blue-black, IrS_2 brown.

(3) $IrCl_3$, olive-green and insoluble (even in aqua regia), is formed by heating $(NH_4)_2IrCl_6$ in chlorine at 440°. Green salts $M^I_3[Ir^{III}Cl_6]$ are formed by heating $M^I_2IrCl_6$ in HCl gas. Ir_2O_3 is black, $Ir(OH)_3$ green, Ir_2S_3 and $Ir(HS)_3,2H_2O$ are brown. Green $Ir_2(SO_4)_3$ and yellow alums (green when anhydrous) $M^IIr(SO_4)_2$, $12H_2O$ with K, NH_4, Rb, Cs, Tl^I are known, also complex cyanides $M_3{}^IIr(CN)_6$ (colourless) and the free acid $H_3Ir(CN)_6$ (white). $K_3Ir(NO_2)_6$ is white and soluble in hot water.

(4) IrF_4 is a brown oil, $IrCl_4$ a reddish-black solid formed by evaporating $(NH_4)_2IrCl_6$ with aqua regia; K_2IrCl_6 (dark red, sparingly soluble), Na_2IrCl_6 (black, readily soluble) are formed by heating iridium with the alkali chloride in chlorine and crystallising, and $(NH_4)_2IrCl_6$ (reddish-black, sparingly soluble) by precipitating Na_2IrCl_6 solution with NH_4Cl. $IrCl_4$ gives a red solution, reduced by H_2S to an olive-green solution of $IrCl_3$. Addition of KOH solution to $IrCl_4$ solution precipitates dark red K_2IrCl_6, soluble in excess to an olive-green solu-

tion ; on warming this becomes bright green, rose-red, and violet, and intensely blue $Ir(OH)_4$ precipitates. From these colour changes iridium got its name (Greek *iris*, the rainbow). Black IrO_2 is formed on heating iridium powder in oxygen at 1070°.

(5) White IrF_5 and dark green RuF_5 are the most definite 5-valent compounds in the series of platinum metals.

(6) Yellow IrF_6, m.p. 44°, is very reactive. Impure blue IrO_3 is formed by fusing iridium with potassium nitrate and extracting with water.

Palladium

Palladium was discovered by Wollaston in 1803, who advertised it for sale by an anonymous leaflet. Chenevix, who bought the whole stock, concluded that it was platinum amalgam. After Chenevix's paper (which passed through Wollaston's hands as Secretary of the Royal Society) was printed, Wollaston published a full account of palladium in the *Philosophical Transactions* in 1804 : it is difficult to understand this procedure.

Palladium occurs alloyed with gold as *porpesite* and is contained in native platinum. The chief source is the Sudbury (Ontario) nickel ore. Palladium is separated by precipitation as $Pd(CN)_2$ by mercuric cyanide, as PdI_2 by potassium iodide, as $[Pd(NH_3)_2Cl_2]$ with ammonia, or as the compound with dimethylglyoxime (existing in *cis* and *trans* forms, p. 216). On igniting any of these the metal is formed. It is silver-white, ductile and malleable, has a low m.p. (1553°) for a platinum metal, and can be welded at a red heat. Its occlusion of hydrogen (p. 288) is notable. Palladium oxidises to a blue film of PdO on heating in air and the molten metal " spits " from evolution of oxygen like silver. It burns to PdS in sulphur vapour, is soluble in concentrated nitric acid forming brownish-yellow **palladous nitrate** $Pd(NO_3)_2$ and in boiling concentrated sulphuric acid forming reddish-brown **palladous sulphate** $PdSO_4$.

Palladium is used for jewellery and a white alloy with gold (" rhotanium," " palau ") as a substitute for platinum (*Ind. Eng. Chem.*, 1917, **9**, 590 ; 1919, **11**, 570). It amalgamates fairly easily.

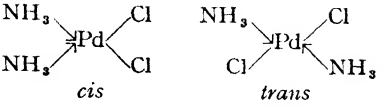
Palladium dissolves in aqua regia to $H_2Pd^{IV}Cl_6$ but on evaporation this forms $PdCl_2$, which also sublimes on heating the metal in chlorine. It is tarnished by iodine vapour. $PdCl_2$ solution is reduced by CO to a black precipitate of the metal (test for CO). Silver nitrate precipitates $Ag_2[PdCl_2(OH)_2]$ from $PdCl_2$ solution.

Palladium shows valencies of 1, 2, 3 and 4, but the bivalent compounds are commonest and most stable.

(1) PdCl (by heating $PdCl_2$), Pd_2S (perhaps $Pd_4S + S$), and the strongly reducing solution, probably containing $KPd^{I}(CN)_2$ or $K_2Pd^{I}(CN)_3$, formed by reducing $K_2Pd^{II}(CN)_4$ solution with sodium amalgam (Manchot, 1930).

(2) $PdCl_2$ is dark red and forms red or brown complex salts $M_2^{I}Pd^{II}Cl_4$ with K, NH_4, Rb, Cs. Black PdO is formed by heating the spongy metal at 800° in oxygen, or by carefully heating the nitrate or boiling its solution. It is a powerful oxidising agent. The precipitated cyanide $Pd(CN)_2$ dissolves in KCN solution and forms crystals of $K_2Pd(CN)_4,3H_2O$. $K_2Pd(NO_2)_4$ is not precipitated by $Hg(CN)_2$. Black PdS is formed from the elements on heating or as a precipitate (insoluble in yellow ammonium sulphide) by H_2S. Brown PdS_2 is precipitated by acid from a solution of Na_2PdS_3 (formed by fusing PdS, S and Na_2CO_3).

A large number of complex compounds of bivalent Pd are known : the three forms of $Pd(NH_3)_2Cl_2$ may be mentioned :

pink $[Pd(NH_3)_4][PdCl_4]$ yellow 

(3) Black PdF_3 is formed by the action of fluorine on Pd or $PdCl_2$. No $PdCl_3$ is known but unstable green $Rb_2Pd^{III}Cl_5$ and $Cs_2Pd^{III}Cl_5$ are formed from hydrated Pd_2O_3, HCl gas and RbCl or CsCl in ether at $-80°$. A black $Pd(NH_3)_2Cl_3$ may be binuclear and contain Pd^{II} and Pd^{IV} rather than Pd^{III} (Mann and Purdie, *J.C.S.*, 1936, 873). Brown Pd_2O_3,xH_2O is formed by electrolytic oxidation of $Pd(NO_3)_2$ solution (Wöhler and Martin, 1908).

(4) No simple PdX_4 halides are known, but brown, red or yellow $M_2^IPd^{IV}Cl_6$ and black $M_2^IPd^{IV}Br_6$, isomorphous with the Pt^{IV} compounds but much less stable, are formed by the action of halogens on the $M_2^IPd^{II}X_4$ compounds. The compounds $[PdCl_4(NH_3)_2]$, $[PdCl_4$ en] are not stable. Brown hydrated PdO_2 is precipitated by alkali from K_2PdCl_6 or formed by anodic oxidation of $Pd(NO_3)_2$ solution : it easily decomposes into PdO and oxygen and is reduced by H_2O_2.

Platinum

Platinum is tin-white and has a high density and m.p. It can be welded at a bright red heat and can be rolled into foil or drawn into wire.

Very thin wires (*Wollaston wires*), down to 0·001 mm. diam., are drawn inside a silver sheath, which can be dissolved off in dilute nitric acid or by making the wire the anode in potassium argentocyanide solution.

Platinum volatilises slightly in air above 800°, especially if it contains iridium, but is more stable if alloyed with rhodium. It is attacked by carbon and phosphorus at a red heat, becoming brittle.

A smoky flame should not be used with platinum crucibles, nor magnesium pyrophosphate ignited along with filter paper, when phosphorus is set free. Easily reducible metals such as tin and lead form fusible alloys with platinum, and their compounds must not be heated with filter paper in platinum crucibles. Platinum is attacked by fused alkalis, sodium peroxide, alkali sulphides, cyanides and nitrates, and fused lithium and magnesium chlorides ; it is only slightly attacked by fused alkali carbonates and not by hydrofluoric acid.

Platinum has the same coefficient of expansion as glass, and may be sealed into this without cracking. Wires in electric lamp bulbs were formerly of platinum, but are now of manganin, or copper coated with boron trioxide, or *kovar*, an alloy of iron, cobalt, nickel and manganese. Platinum is used in jewellery, especially as a setting for diamonds, and in dentistry. It is used for chemical apparatus, as contacts in electrical apparatus and as a catalyst. Tantalum has been proposed as a substitute.

Platinum sponge is a grey porous form obtained by heating ammonium chloroplatinate. *Platinum black* is a finely divided powder obtained by reducing a solution of chloroplatinic acid by zinc or with sodium formate solution. These forms are catalytically very active. *Platinised asbestos* is made by soaking

asbestos fibres (previously boiled with concentrated hydrochloric acid) in platinic chloride solution, drying, and heating in a crucible with a little ammonium chloride, or reducing with sodium formate solution. *Colloidal platinum* is formed as a brown solution by causing small electric arcs to pass repeatedly between platinum wires under water.

Pure platinum is not attacked by hot concentrated hydrochloric, nitric and sulphuric acids, but the last dissolves the commercial metal slightly. It dissolves in hot aqua regia, especially with an excess of concentrated hydrochloric acid. An alloy of platinum and lead dissolves in nitric acid. On evaporating the solution of platinum in aqua regia, moistening the residue with concentrated hydrochloric acid and re-evaporating, reddish-brown deliquescent crystals of **chloroplatinic acid,** $H_2PtCl_6,6H_2O$, commonly called " platinum chloride," are obtained. From this all the other platinum compounds are usually prepared.

The coordination numbers (maximum covalencies) of *platinous* and *platinic compounds* are 4 and 6, respectively. The simple compounds are usually covalent, *e.g.* $PtCl_4$ on solution forms $H_2[PtCl_4(OH)_2]$ and not the $Pt^{\cdots\cdot}$ ion.

The complex cations are stable, *e.g.* $[Pt\,en_3]^{\cdots\cdot}$ of which optically active forms exist, showing that the valency arrangement is octahedral. The simple platinous compounds are often sparingly soluble, but numerous soluble complex compounds exist, *e.g.* K_2PtCl_4, and in this case the valency arrangement is planar (p. 220). Salts of oxyacids are uncommon with most platinum metals except in lower valency stages, but $Pt(SO_4)_2$, $Pt(NO_3)_4$ and many complex compounds (including carbonates), *e.g.* $[Pt(NH_3)_6](SO_4)_2,H_2O$, $[Pt(NH_3)_6](NO_3)_4$ and $[Pt(NH_3)_6](CO_3)_2$ are known.

Chloroplatinic acid is a strong dibasic acid: $H_2PtCl_6 \rightleftharpoons 2H^{\cdot} + PtCl_6''$. On electrolysis of its solution platinum black is deposited on the cathode by reduction by nascent hydrogen. The lithium $Li_2PtCl_6,6H_2O$ and sodium $Na_2PtCl_6,6H_2O$ salts are soluble, the potassium K_2PtCl_6 and ammonium NH_4PtCl_6 salts form yellow precipitates and the rubidium and caesium salts are even less soluble. The salts decompose on heating: $K_2PtCl_6 = Pt + 2KCl + 2Cl_2$ (the ammonium salt leaves a residue of platinum). Silver nitrate gives with a solution of the acid or the sodium salt a yellow precipitate of Ag_2PtCl_6 which is decomposed by boiling water; the filtrate deposits crystals of $PtCl_4,5H_2O$ or $H_2PtCl_4(OH)_2,3H_2O$ on evaporation:

$$Ag_2PtCl_6 + 2H_2O = H_2PtCl_4(OH)_2 + 2AgCl.$$

Platinic chloride $PtCl_4$ is a reddish-brown crystalline mass formed when H_2PtCl_6 is heated in chlorine at 369° or in hydrogen chloride at 165°:

$$H_2PtCl_6 = PtCl_4 + 2HCl.$$

It forms a yellowish-red solution containing $H_2[PtCl_4(OH)_2]$. Potassium iodide does not precipitate K_2PtCl_6 from a solution of H_2PtCl_6 but gives a clear dark wine-red solution, which on boiling gives a black precipitate of **platinic iodide** PtI_4, soluble in alcohol. With hydriodic acid this iodide forms reddish-black very soluble needle-shaped crystals of **iodoplatinic acid** $H_2PtI_6,9H_2O$, which

forms soluble salts, *e.g.* K_2PtI_6. On heating, PtI_4 forms successively PtI_3, PtI_2 and Pt, with evolution of iodine.

Platinic oxide (or **platinum dioxide**) PtO_2 is obtained as a black powder by adding sodium carbonate to H_2PtCl_6 solution, evaporating, extracting the residue with acetic acid and gently heating the insoluble reddish-brown **platinic hydroxide** (really the complex $H_2[Pt(OH)_6]$):

$$H_2PtCl_6 + 3Na_2CO_3 + 3H_2O = H_2[Pt(OH)_6] + 6NaCl + 3CO_2;$$

$H_2[Pt(OH)_6] = PtO_2 + 4H_2O$. Platinic hydroxide dissolves in hydrochloric acid to $H_2[PtCl_4(OH)_2]$ and in potassium hydroxide solution to **potassium platinate**, forming golden-yellow hexagonal crystals $K_2[Pt(OH)_6]$ isomorphous with the stannate $K_2[Sn(OH)_6]$ (see p. 519). Silver nitrate gives a yellowish-white precipitate of $Ag_2[Pt(OH)_6]$ from a solution of the potassium salt. On heating, PtO_2 forms Pt_2O_3, PtO and finally platinum.

Tervalent platinum compounds are the greenish-black **trichloride** $PtCl_3$ formed by heating $PtCl_4$ in chlorine at 390°, the dark brown **sesquioxide** Pt_2O_3, the yellow **tricyanide** $Pt(CN)_3$ formed by heating $H[Pt^{III}(CN)_4],2H_2O$ (the salts of which are formed by oxidising platinocyanides with H_2O_2), and several complex ions.

The compounds of **bivalent platinum** are important. The brownish-green **platinum dichloride** $PtCl_2$ is formed by heating $PtCl_4$ in chlorine at 580°. It is insoluble in water but dissolves in hydrochloric acid to form the dark brown **chloroplatinous acid** H_2PtCl_4, also formed by the action of sulphur dioxide on a solution of H_2PtCl_6. Although it does not crystallise but gives an amorphous solid on evaporation, it forms crystalline **chloroplatinites**, *e.g.* dark red crystals of K_2PtCl_4, also obtained by warming a paste of K_2PtCl_6 with cuprous chloride and used in photography. **Platinous iodide** PtI_2 is formed as a black powder by heating $PtCl_2$ with potassium iodide solution.

On heating with dilute alkali K_2PtCl_4 forms black **platinous hydroxide** $Pt(OH)_2$, soluble in hydrochloric acid. It may be $H_2[Pt(OH)_4]$ although it has no acidic properties. On gentle heating it forms black **platinous oxide** PtO. **Platinum sulphide** PtS is a black powder formed by heating PtS_2 at 630°. It forms a face-centred tetragonal lattice with PtS_4 groups.

Platinum disulphide PtS_2 is formed by the action of hydrogen sulphide on hot H_2PtCl_6 solution as a black precipitate, soluble in yellow ammonium sulphide to a solution which may contain a **thioplatinate**.

An important compound of bivalent platinum is **barium platinocyanide** $Ba[Pt(CN)_4],4H_2O$, a lemon-yellow powder used for fluorescent screens for X-rays and prepared by warming H_2PtCl_6 with baryta water and hydrocyanic acid, passing in sulphur dioxide till colourless, filtering from $BaSO_4$ and crystallising:

$$H_2PtCl_6 + 5Ba(OH)_2 + 4HCN + SO_2 = BaPt(CN)_4 + BaSO_4 + 3BaCl_2 + 8H_2O.$$

The free acid $H_2[Pt(CN)_4],5H_2O$ is known. $Mg[Pt(CN)_4],3\frac{1}{2}H_2O$ is bright scarlet with green and purple reflected colours, but forms white $Mg[Pt(CN)_4]$, $2H_2O$ at 100°.

Platinum trioxide PtO_3, the only known compound of 6-valent platinum, is a brown powder (which does not form hydrogen peroxide with acids), obtained by

electrolysing a cooled solution of potassium platinate $K_2[Pt(OH)_6]$ in potassium hydroxide, and extracting the yellow deposit of $K_2O,3PtO_3$ on the anode with ice-cold dilute acetic acid. It liberates chlorine from dilute hydrochloric acid.

The numerous complex **coordination compounds** formed by 2- and 4-valent platinum have been briefly reviewed on p. 214.

The Inert Gases

The inert gases form Group VIII *b* when they are regarded as closing a period, which is in conformity with their atomic structure (p. 209). They bridge the gap between the strongly electropositive elements of Group I and the strongly electronegative elements of Group VII.

The alkali metals in Group I have an inert gas structure in the shell immediately below the single valency electron in the outer shell, and behave as strongly electropositive elements, as they tend to lose this valency electron to form an ion with the inert gas structure, lithium ion having the helium structure (2 electrons) and all the other ions a complete outer shell of 8 electrons. The halogens in Group VII have 7 valency electrons and behave as strongly electronegative elements, as they tend to complete an inert gas grouping of 8 electrons either by gaining an electron to form a univalent ion, or by attracting and sharing an electron with another atom to form a covalent link (p. 213).

Since the inert gases have completed groups (2 or 8) of very firmly bound electrons they show no tendency to gain or lose electrons, *e.g.* to form ions (except gaseous ions in electrical discharge tubes), and as their electron groups cannot expand they form no ordinary covalent links. The only possibility of compound formation is the *donation* of electron pairs by their atoms to form coordinate links. Argon, krypton and xenon do this in forming crystalline hydrates with $6H_2O$ when they are compressed with water and the pressure released.

The most stable hydrate is of xenon, with the fairly small dissociation pressure of 1·15 atm. at 0°. Supposed compounds of helium with mercury, and of krypton with bromine, are non-existent (Yost and Kaye, *J.A.C.S.*, 1933, **55**, 3890; Ruff and Menzel, 1933), but compounds of argon with 1, 2 (the most stable), 3, 6, 8 and 16 molecules of boron trifluoride are described (Booth and Willson, *J.A.C.S.*, 1935, **57**, 2273). The lower compounds may be formed by coordinate links ($A \rightarrow BF_3$) and the higher by linking of BF_3 molecules together by donation from fluorine to boron if covalent bonds are formed.

That the inert gases are monatomic is shown by the value 1·667 of the ratio of specific heats $\gamma = c_p/c_v$ (p. 33), and less certainly by the refractive indices, etc.

The **emanations** of radium (**radon**, Dorn, 1901), thorium (**thoron**, Rutherford and Soddy, 1900) and actinium (**actinon**, Giesel, 1902; Debierne, 1903) are inert gases, since they have no chemical properties although they are radioactive. They are isotopes but have different radioactive constants. Since the inert gases are devoid of chemical properties they are completely described by

their physical properties, given in the table below (Moureu, *J.C.S.*, 1923, **123**, 1905; Allen and Moore, *J.A.C.S.*, 1931, **53**, 2512, 2532). They are best characterised by their spectra, excited in discharge tubes.

	Helium	Neon	Argon	Krypton	Xenon	Radon
At. no. - -	2	10	18	36	54	86
Electron config. -	2	2·8	2·8·8	2·8·18·8	(28)18·8	(60)18·8
Normal density -	0·17846	0·89990	1·78364	3·743	5·896	9·97
Crit. temp. -	− 267·90°	− 228·70°	− 122·44°	− 62·5°	+ 16·6°	104·5°
Crit. press. (atm.)	2·26	26·86	47·996	54·3	58·2	62·4
B.p. - - -	− 268·87°	− 245·92°	− 185·85°	− 152·9°	− 107·1°	− 62°
M.p. - - -	− 272°	− 248·52°	− 189·25°	− 157°	− 111·5°	− 71°
Compressibility λ	− 0·0005	− 0·0004	+ 0·001	+ 0·002	+ 0·006	+ 0·018
Abs. coeff. in H_2O at 0° - -	0·00967	0·0114	0·0053	0·1105	0·242	0·51

Argon

Since argon was the first inert gas discovered and is the commonest, it will be dealt with first.

Cavendish, in 1785, in his attempts to find if atmospheric nitrogen is all of one kind, noticed that when it is sparked with oxygen over alkali solution, and the excess of oxygen is absorbed by alkali sulphide (p. 562), a small residue of gas remains. This result attracted no attention until Lord Rayleigh in 1892 showed by accurate density determinations that atmospheric nitrogen is 0·1 p.c. heavier than nitrogen prepared from ammonia. Later experiments showed that the normal density of atmospheric nitrogen is 1·2572 g./lit., that from oxides of nitrogen reduced by heated iron, from ammonium nitrite and from urea and sodium hypobromite 1·2505 g./lit. Cavendish's experiment was confirmed, and the spectrum of the small unabsorbed residue was found to be different from that of nitrogen. The presence of a new gas denser than nitrogen was suspected. This was isolated by Rayleigh and Ramsay in 1894 (*Phil. Trans.*, 1895, **186**, 187; *J.C.S.*, 1895, **70**, ii, 99; Ramsay, *Gases of the Atmosphere*, 4th edit., 1913; Travers, *The Discovery of the Rare Gases*, 1928) by two methods: (i) absorption of nitrogen by red-hot magnesium (Ramsay), (ii) conversion of nitrogen into oxides by sparking with oxygen in presence of alkali solution (Rayleigh; this is Cavendish's original method).

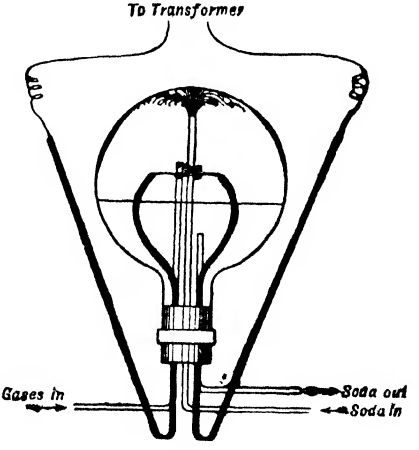


FIG. 344.—Rayleigh's method for the preparation of argon.

(1) The oxygen was absorbed by passing pure dry air over red-hot copper and the nitrogen by passing repeatedly over red-hot magnesium. The nitrogen was slowly absorbed as magnesium nitride Mg_3N_2. The volume of gas was reduced to $\frac{1}{80}$th and further treatment raised its density to 19·94 (H = 1).

(2) A mixture of 11 vols. of oxygen and 9 vols. of air was passed into a 50 lit. glass globe in which a transformer discharge of 6000–8000 volts was passed between heavy platinum electrodes (Fig. 344). A fountain of sodium hydroxide solution was discharged over the inside of the globe (Rayleigh, *J.C.S.*, 1897, **71**, 181). With a consumption of energy of 1 horse-power, 20 lit. of gas were absorbed per hour. The residual oxygen was absorbed by alkaline pyrogallol.

The new gas was chemically inert. It was not absorbed by heated metals, copper oxide, caustic alkali, potassium permanganate, sodium peroxide, phosphorus, etc., nor did it react when sparked with oxygen, hydrogen, chlorine, or even fluorine. It was unchanged by an electric arc maintained for several hours. Hence it was called **argon** (Greek *argon*, lazy or inactive).

Since argon is used for filling metal filament lamps to delay the blackening of the glass bulb by volatilised tungsten, it is made technically.

It was formerly obtained by circulating air over a mixture of calcium carbide and 10 p.c. of calcium chloride heated at 800° in iron retorts, when nitrogen is absorbed as calcium cyanamide and oxygen as calcium carbonate ; the residual gas was passed over heated copper oxide to oxidise carbon monoxide to dioxide, which was absorbed by alkali, and was then dried. The oxygen may also be removed by passing over heated copper, or by burning with hydrogen, and the residual gas passed over heated calcium carbide.

Argon is now made by the *fractional distillation of liquid air*. As the b.ps. are N_2 −196°, A −186°, O_2 −183°, the argon tends to accumulate in the liquid oxygen, from which it is separated by fractionation.

In the Linde process (Fig. 345) the crude liquid oxygen from the first fractionating column (not shown), which contains some nitrogen and 4–5 p.c. of argon, is fed at *A* into the centre of a second column, in the upper part of which is a nest of tubes *B* cooled in a bath of liquid nitrogen. Liquid oxygen drains into *M* and is evaporated by the heat of compressed air passing into a spiral tube at *F*, pure oxygen gas passing out at *C*. The gas rising through the column contains argon and nitrogen, and some oxygen not scrubbed out. It passes through the cooler *B* and leaves this containing equal amounts of argon and nitrogen and about 10 p.c. of oxygen. This gas passes at *D* to the centre of a third column ; from this pure nitrogen gas leaves through the upper nest of tubes *H* cooled in liquid nitrogen, and a liquid mixture of argon with some

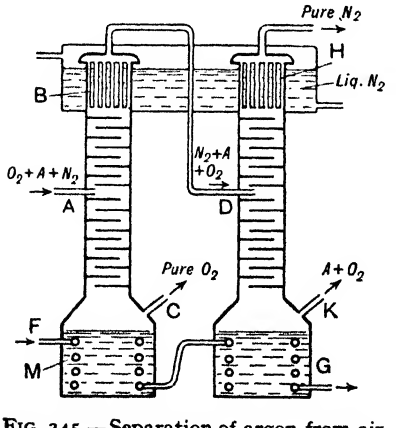


FIG. 345.—Separation of argon from air.

oxygen and a little nitrogen drains into *G*, where it is evaporated by a compressed air coil, and the gas leaves at *K*. The oxygen is removed from this gas by passing over red-hot copper.

Commercial argon (90-95 p.c. A and the rest nitrogen) is used for lamp filling. By special methods a gas containing 99·5 p.c. A, 0·5 p.c. N_2 and less than 0·1 p.c. O_2 can be prepared. The last traces of nitrogen and oxygen can be removed by striking an arc between a tungsten electrode and a pool of fused mixed metal (p. 434) in a bulb of the gas. Traces of other inert gases are still present.

Helium

In 1868 the spectroscopic examination of the chromosphere of the sun during a total eclipse revealed a new yellow line, called D_3, and Lockyer concluded that it corresponded with an element to which he gave the name helium (Greek *helios*, the sun). In 1894 Ramsay (*J.C.S.*, 1895, **67**, 1107) at the suggestion of Miers examined the gas evolved from *cleveite* (a variety of pitchblende) by heating with dilute sulphuric acid, or in vacuum, which had been supposed by Hillebrand (1888) to be nitrogen. It contains about 20 p.c. of nitrogen, but by sparking with oxygen over alkali there was a residue, found by Crookes to give the D_3 spectrum line.

Ramsay and Travers in 1897 showed by exhaustive fractional diffusion that the gas could be separated into a light fraction, showing all the properties of helium and unaffected by further diffusion, and a heavier fraction containing argon.

Helium occurs only in traces (0·0005 vol. p.c.) in the atmosphere, but can be separated technically by fractionation. It is contained occluded in uranium minerals (in which it results from radioactive changes, p. 202) and is found in the gases from many mineral springs (Bath, Cauterets, etc.).

Inert gases are evolved from hot-springs having their sources at great depths in the earth (Moureu, *J.C.S.*, 1923, **123**, 1905). The Bourbon-Lancy spring evolves 16,000 lit. of inactive gas per annum, of which 10,000 lit. are helium. Some springs yield gas containing 10 p.c. of helium, but usually the amount is much smaller. The water of these springs is slightly radioactive, but according to Moureu this has nothing to do with the inert gases. Rayleigh and Ramsay found that the gas evolved on heating rain water contains twice as much argon as air (cf. Travers, *J.C.S.*, 1937, 1561).

The most important source of helium is the *natural gas* (mostly methane) from some petroleum springs and other sources in Texas, Utah and Colorado in the U.S.A., and Medicine Hat in Canada. Some contain 8 p.c. by vol. of helium but less than 1 p.c. is usual. Since the gas is free from hydrogen and neon (of low b.ps.) the helium is obtained from it simply by strong cooling, when the other gases present (of much higher b.ps.) condense, leaving helium gas (McLennan, *J.C.S.*, 1920, **117**, 923; Moore, *Nature*, 1923, **111**, 887).

Sources of helium attracted attention in view of the use of this gas in place of hydrogen for filling the gas containers of airships. It is also proposed to use a mixture of oxygen and helium instead of air in diving apparatus since helium

does not appreciably dissolve in the blood under pressure. Nitrogen dissolves and is liberated in bubbles in the blood when the pressure is released, giving rise to "caisson disease." In the United States a considerable amount of helium extracted from natural gas is available. An alternative source is *monazite* (p. 534), found in large amounts at Travancore, India. It contains about 1 c.c. of helium per g., formed from radioactive changes of thorium (p. 202), and this is evolved on heating.

Helium is the least soluble of all gases and the most difficult to liquefy. It is easily purified by contact with coconut charcoal at liquid air temperature, which adsorbs all gases except helium, and hydrogen and neon, which are not usually mixed with the helium (Dewar, 1904). Quartz at 1100° is permeated only by hydrogen and helium; helium can diffuse through glass at room temperature (Paneth, 1928).

Liquid helium was obtained by Kamerlingh Onnes in 1907 by the Joule-Thomson expansion of the gas previously cooled to 15° abs., since its inversion point (p. 40) is at a very low temperature. The colourless liquid has the very low density of 0·122 and boils at only 4° above absolute zero. By rapid evaporation the temperature was reduced to 0·82° abs., but the helium was still liquid. **Solid helium** was obtained by Keesom in 1926 by cooling the liquid to 1° abs. *under pressure.*

The m.p. curve at very low temperatures is almost parallel to the temperature axis and does not cut the vapour pressure curve of the liquid. Helium has no triple point and the solid phase is not stable at any temperature under its own vapour pressure, but only at higher pressures, *e.g.* 26 atm. at 1° abs. and 813 atm. at 12° abs.

There are two forms of liquid helium, He-I and He-II, with a transition point (λ-point). They differ in density, specific heat, and dielectric constant. Liquid helium has a very flat meniscus and low surface tension and creeps over glass in a remarkable way.

Neon

Ramsay in 1896 suggested that helium and argon are two members of a new ("zero") group in the Periodic System and that three other inert gases should exist to complete it.

In the residue from the evaporation of liquid air Ramsay and Travers in 1898 discovered two new inert gases, **krypton** (Greek, *krypton*, concealed) and **xenon** (Greek, *xenos*, the stranger), and in 18 lit. of crude liquid argon they found helium and a new inert gas **neon** (Greek *neon*, new). Examination of the residues from the evaporation of 120 tons of liquid air failed to indicate the presence of any other inert gases (*Proc. Roy. Soc.*, 1901, **67**, 329).

Helium and neon, with low b.ps., remain gaseous in the column where liquid nitrogen collects in air fractionation. The gas is passed through a spiral tube in the upper part of the column, strongly cooled by liquid nitrogen, when much of the nitrogen condenses. The gas then contains helium, neon and about 50 p.c. of nitrogen which can be removed by chemical absorption, leaving a mixture of

1 vol. of He and 3 vols. of Ne. By cooling this with liquid hydrogen, neon containing only 0·2 p.c. of He solidifies. It can also be separated by adsorption on charcoal cooled in liquid air.

Air contains 0·0018 vol. p.c. of neon and a Claude liquefier making 50 cu. m. of oxygen per hour produces 100 lit. of neon per day, the commercial gas containing about 2 p.c. of helium.

In an electrical discharge tube at about 2 mm. pressure neon gives a beautiful orange-red light which is extensively used in various types of illumination. With mercury vapour and neon or argon a blue or green coloured discharge results, the " ripple " effect being produced by a trace of an organic compound. An orange light results when a tube of neon at atmospheric or lower pressure, containing some mercury, is shaken (Collie, 1909).

Krypton and Xenon

Krypton (0·0001 vol. p.c.) and **xenon** (0·000009 vol. p.c.) are present only in traces in air, but can be separated by the fractionation of crude argon (Allen and Moore, *J.A.C.S.*, 1921, **53**, 2512, 2522). The lower boiling fraction is argon, the middle is krypton, and the higher is xenon. Selective adsorption on charcoal may also be used (Valentiner and Schmidt, 1905) ; if the charcoal bulb is warmed to $-80°$ pure krypton is evolved, at higher temperatures krypton and xenon. This gas is recondensed on charcoal at $-150°$ and the bulb connected with a second charcoal bulb cooled to $-180°$, when krypton passes over into this leaving xenon in the first bulb.

In another method (Lepape, 1928) the gas evolved by the slow evaporation of commercial liquid oxygen in a 2-lit. vacuum flask passes through a tube containing coconut charcoal and immersed in the liquid oxygen : the yield is 85 c.c. of Kr and 0·8–20 c.c. of Xe which can be separated by fractional adsorption as described.

Krypton would be superior to argon for gas-filled lamps and is used in some discharge tubes, giving a green or lilac light. Xenon gives a blue or (with a higher potential) green light.

INDEX

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