CHEMICAL PRINCIPLES

BOOKS BY JOHN H. YOE

Chemical Principles

With particular application to qualitative analysis. 311 pages. 6 by 9. 29 figures, 2 colored plates. Cloth.

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CHEMICAL PRINCIPLES

WITH PARTICULAR APPLICATION TO QUALITATIVE ANALYSIS

BY

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PREFACE

Qualitative analysis is both an art and a science. Perhaps no better approach to the advanced courses in chemistry can be taken than via the qualitative laboratory. Here, the student has an opportunity to develop his technique in carrying out not-too-complicated chemical operations and at the same time to study at first hand many of the fundamental principles of chemistry. Such a course should serve the dual purpose of reviewing and expanding the student's knowledge of general chemistry and of preparing him for more advanced courses, especially physical or theoretical chemistry. In other words, such a course should serve as "a bridge to span the widening gap" between the first-year course in chemistry and theoretical chemistry. The purpose of this book is to serve as an adjunct to such a course. It may be used with any of the numerous good laboratory manuals on qualitative analysis.

The first four chapters are intended to furnish a brief review of certain ideas and fundamental laws treated in general chemistry, and they were purposely made elementary and concise. Very little classroom time should be devoted to these chapters; if desired, they may be assigned for home work only, the regular course work starting with oxidation-reduction reactions in Chapter V.

Chapters VI to X are devoted to gases, liquids, solids, solutions, and electrolytes, followed by a study of chemical equilibrium (homogeneous and heterogeneous) in Chapters XI and XII.

Chapters XIV to XIX deal with applications of the law of chemical equilibrium to the various types of equilibria encountered in qualitative analysis. Illustrative problems are solved for each type of equilibrium, and many additional problems are given (with answers) for home and class work. As it is necessary that the student be thoroughly familiar with the units of weight, volume, and concentration used in equilibria calculations, these terms are reviewed in Chapter XIII just before the latter are taken up. It is a good plan to have the students record all their problem work in a notebook which is submitted once a week for inspection and grading.

On account of the importance of the hydrogen-ion concentration, not only in chemistry but also in the biological and medical sciences, this subject is treated in considerable detail (Chapter XVIII). Classroom demonstration of the colorimetric method of *p*H determination should be made with several indicators suitable for the acid, neutral, and alkaline range, respectively. The indicator color chart (page 193) is given simply by way of illustration and of course should never be used as a substitute for the actual colored solutions.

Chapters XX to XXII serve as a brief introduction to a number of topics which will be treated in more detail in physical chemistry. Colloids form the subject for the concluding chapter (XXIII). In view of the importance of this subject, not only to students who are going on with chemistry but also to those who plan to go into biology, medicine, and other sciences, Chapter XXIII has been made relatively detailed. It is hoped that this chapter will give the student a clear understanding and appreciation of matter in the colloid state and of the importance of colloid chemistry, from both a theoretical and a practical standpoint.

Of special interest to the student in qualitative analysis is the Appendix dealing with dry methods of analysis, which are so useful to the mineralogist and the geologist. If time permits, two or three laboratory periods may well be devoted to these simple, rapid, and interesting methods for the detection and identification of substances.

Permission to quote or to reproduce certain data and cuts from the following works is gratefully acknowledged: Getman and Daniels' "Outlines of Theoretical Chemistry," fifth edition, and Bass' translation of Schwarz's "Chemistry of the Inorganic Complex Compounds," both published by John Wiley & Sons, Inc.; Kendall's "Smith's Inorganic Chemistry" and Fales' "Inorganic Quantitative Analysis," both published by D. Appleton-Century Co.; Bancroft's "Applied Colloid Chemistry," published by McGraw-Hill Book Co.; Taylor's "Chemistry of Colloids," second edition, published by Longmans, Green & Co.; Hatschek's "Physics and Chemistry of Colloids" and Rice and

Cortelyou's "Popoff's Quantitative Analysis," third edition, both published by P. Blakiston's Son & Co., Inc.; and Taylor and McCrumb's "ABC of *p*H Control," sixth edition, published by LaMotte Chemical Products Co. Also, several cuts were furnished by the LaMotte Chemical Products Co. In addition to these publications, many standard chemical works and periodicals were consulted during the preparation of the manuscript, and I gladly acknowledge these sources of aid.

To Mr. Hugh N. Dyer, Jr., is due thanks for checking all the problems and answers and for reading the entire manuscript. Professor Arthur F. Benton read certain portions of the manuscript and made helpful criticisms, for which I desire to express my appreciation. Françoise Cheely Yoe, my wife, typed the manuscript and assisted with reading the proof. I am very grateful for this assistance.

Although much effort has been made to have the book free of mistakes, it is recognized that some errors may be found. I shall be obliged to any one who is kind enough to call such mistakes to my attention. Also, criticisms and suggestions will be welcomed.

UNIVERSITY OF VIRGINIA
October, 1936

J. H. Y.

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CHEMICAL PRINCIPLES

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CHAPTER I

INTRODUCTION

The origin and meaning of the word **chemistry** are not known. It is certainly very old, probably as old as civilization itself. Some claim that it refers to the ancient land of Chemî (Egypt). Others believe that it is derived from the Greek word χημεία, which means a mingling or an infusion, and that it refers to the art of extracting and mixing plant juices for use as medicines, practiced by the ancient priests. About the middle of the seventh century the Arabians overran Egypt and learned something of this art from the Egyptians. They prefixed the Arabic article **al** to **chemia,** whence the word **alchemy.** The object of alchemy was to transmute the baser metals into gold and silver and to find a means of healing diseases and to prolong life.

Ancient records and objects found in excavations show that ancient peoples knew how to work gold, silver, copper, and iron. They were also acquainted with the art of making glass, pottery, enamels, alloys, artificial gems, dyes, paints, and medicines. Wine, salt, vinegar, and other products were known to the ancients.

During the fourteenth century alchemy spread over the civilized world, and by the sixteenth century it began to be replaced by another era known as the iatrochemical or medical chemistry age, which lasted up to the end of the seventeenth century when the philosopher, Robert Boyle (1627–1691), placed chemistry on a truly scientific basis. In 1774, Priestley discovered oxygen, and a few years later the brilliant French chemist, Lavoisier, began his classical experiments to show the relation of oxygen to air. The discovery of oxygen and the researches of Lavoisier mark a new era in chemistry. In fact, Lavoisier is often called "the father of modern chemistry." With the introduction of the chemical balance, chemistry made great strides as an exact science.

We may define chemistry as the science which deals with the nature of elements and compounds. As a matter of convenience, chemistry has been divided into a number of fields, for example: inorganic chemistry, organic chemistry, analytical chemistry, physical chemistry, biochemistry, industrial chemistry, etc. In the pages that follow, we shall be concerned chiefly with chemical principles and their application to the subdivision of analytical chemistry known as qualitative analysis.

Physical Chemistry. This division of chemistry deals with the general principles or laws which control chemical phenomena. It summarizes and systematizes the established facts of chemistry and tries to find out the reasons why, and the conditions under which, transformations of matter take place. Hence, this branch of chemistry is often called **theoretical chemistry,** and it is concerned with matter, electricity, and radiation, the units of which are the **atom,** the **electron,** and the **quantum,** respectively.

Hypothesis, Theory, and Law. An **hypothesis** is a supposition advanced as a basis for reasoning and experimentation or presented as an explanation of certain observed facts. Often it is a mere assumption or guess, which later may be proved erroneous. A **theory** is a more or less verified or established explanation accounting for known facts or phenomena. When an hypothesis assumes a high degree of probability it becomes a theory. A **law** is a condensed statement, or generalization, which sums up all the known facts in a given case. When a law has been exhaustively and critically investigated and has been found valid in every instance, then it may be regarded as tantamount to a **statement of fact.**

THE NATURE OF MATTER

All science is based upon several fundamental concepts: the concepts of matter, of energy, of space, and of time. From these concepts science derives all her descriptions, classifications, hypotheses, theories, and laws. In the physical sciences we are primarily concerned with the concepts of matter and energy. Chemistry deals with matter in all forms, both simple and complex, whether natural or artificial, and with changes in matter. Physics is primarily concerned with the study of energy, but since all matter possesses energy and all changes in matter are accompanied by energy changes, it is obvious that there can be no sharp line of distinction between chemistry and physics. There is much physics in the study of chemistry and much chemistry in the study of physics.

If we grant that matter is an ultimate reality, we can define it only by describing its various forms in terms of those properties recognized by our five senses. The property possessed by all forms of matter is mass, the quantity of matter. Owing to the force of gravitation, any mass can be measured. Any two masses in space tend to move towards each other as if impelled by a force which is directly proportional to the product of their masses and inversely proportional to the square of the distance between them. When we weigh a sample of matter, we simply measure the force between its mass and that of the earth. All matter has weight, but not everything weighable is matter, as modern research has shown that heat, light, and electricity possess some weight. In fact, matter itself is electrical in nature, and we shall probably soon have to revise our conceptions of matter and energy. The Einstein theory of the equivalence of mass and energy was verified in 1935.

Although mass is probably the most important single attribute of matter, it falls far short of describing matter even approximately, for matter also occupies space and may exist in any of three states: solid, liquid, or gaseous. Moreover, since matter may be colored or colorless, may or may not possess an odor, and so on, many properties must be given in order to describe a given sample of matter completely. The object of chemistry is to describe as nearly completely as possible all the known forms of matter and to study changes in the composition of matter. One of the most fundamental laws of chemistry is the **law of conservation of mass** or the **law of indestructibility of matter.** This law states that matter cannot be created nor can it be destroyed, although its form may be changed. In other words, the **total mass** of matter is constant. Many very careful experiments have been made to prove or to disprove this law, but invariably it has been found valid within the limits of experimental error. Every chemical equation is based upon this law, whether dealing with elements or with compounds. We shall, therefore, discuss it more fully in Chapter II, along with the other fundamental laws of chemistry.

THE CHEMICAL ELEMENTS

The ancient conception of an element was quite different from the modern one, although nine substances, now recognized as true elements, have been known and used since the dawn of history; namely, the metals: gold, silver, copper, iron, lead, tin, and mercury, and the non-metals: sulfur and carbon. Empedocles (about 440 B.C.) and Aristotle (384–322 B.C.) taught that matter was of one kind and that the wide variety of matter was due to the greater or less abundance of the four "elements" or "principles," earth, air, water, and fire.

Boyle, in 1661, was the first to define an element clearly. According to him an element is "a substance incapable of decomposition by any means with which we are at present acquainted." In 1789 Lavoisier made a clear distinction between an element and a compound. At that time only twenty-three elements were known. There are now ninety known elements. The last element to be discovered has been named illinium, in honor of the State of Illinois. It was discovered in 1926 by Professor Hopkins at the University of Illinois and also, independently, the same year by Professor Rolla at the Royal University of Florence.

Becquerel (1896) was the first to discover that the elements of highest atomic weights (e.g., uranium) undergo spontaneous disintegration. Man has no control over this process. It is called **radioactivity** and will be treated as a special topic subsequently (see page 256). The radioactive elements decompose into simpler elements; for example, radium spontaneously splits up into a number of other elements such as helium, radon, and lead. Recently some of the lighter elements have been disintegrated artificially. For example, Rutherford and Chadwick (1922) have succeeded in disintegrating nitrogen atoms.

Distribution of the Elements. Of the ninety known elements less than one-fourth are abundant and about one-half are found in substances commonly used in chemical laboratories. The others are rare, and some are very scarce indeed. About twenty of the elements occur in nature in the free state; all others are present in compounds only and must be separated or isolated by special means. Twenty elements constitute 99.5 per cent of the earth's crust; the remaining ones constitute only 0.5 per cent. Oxygen is by far the most abundant of the elements and accounts for about 50 per cent of the earth's crust. Silicon is next in abundance (about 27 per cent), followed by aluminum (nearly 8 per cent) the most abundant metal, and then iron (4.5 per cent). Calcium, magnesium, sodium, and potassium are each present in amounts varying from 2 to 3 per cent. The following are present to the extent of a few tenths of a per cent or less: titanium, hydrogen, carbon, phosphorus, sulfur, barium, manganese, fluorine, and chlorine. Although about four-fifths of the air is nitrogen, this element constitutes only 0.03 per cent of the total composition of the earth, including the solid shell, the oceans and other waters, and the atmosphere. The relative abundance of an element by no means determines its importance or usefulness. Carbon comprises only about 0.2 per cent of the total composition of the earth's crust, yet were it not for this element no life, either plant or animal, could have developed on the earth since carbon is the most important element in all organic compounds. On the other hand, titanium is more than twice as abundant as carbon and has few uses; in fact, it is an objectionable impurity in certain iron ores.

CHAPTER II

FUNDAMENTAL LAWS. ATOMS AND MOLECULES. ATOMIC AND MOLECULAR WEIGHTS. ELECTRONS, PROTONS, AND QUANTA

FUNDAMENTAL LAWS

Law of the Conservation of Mass. In 1756 the Russian chemist Lomonossov heated tin in the presence of air in a closed vessel and found that there was no change in the weight of the system, although the tin was oxidized. Since weight at a given place is a measure of mass or quantity of matter, Lomonossov definitely enunciated the law of the **conservation of mass** or the **law of the indestructibility of matter.** In 1774, Lavoisier made a similar experiment with tin, obtained the same result and arrived at the same conclusion made by Lomonossov. The law of the conservation of mass may be stated as follows: **When a chemical reaction takes place, the total mass of the substances reacting is equal to the total mass of the reaction products,** or otherwise stated, **the mass of a system is unaltered by any chemical change that takes place within it.** Sometimes this law is stated thus: The total mass of the universe is a constant. The objection to this form of statement is that we have no means of verification.

Landolt has subjected the law of the conservation of mass to a very rigid series of experiments which was begun in 1893 and was not completed until 1908. After a careful examination of fifteen different chemical reactions, he failed to detect any variation in weight greater than the experimental error. Every chemical equation is based upon the assumed validity of this law, and hence it is a fundamental law of chemistry.

Law of Definite Proportions. Chemical analyses of many thousands of compounds have shown that each compound is always composed of the same elements united in the same proportions by weight. This is the **law of definite proportions.** It is sometimes called the **law of constant proportions** or the **law of constant composition** and was established by very careful researches by Richter and by Proust about the beginning of the nineteenth century.

Law of Multiple Proportions. John Dalton discovered that elements may unite in more than one proportion by weight. For example, he found by analysis that methane and ethylene contain carbon and hydrogen in the ratios of 6 : 2 and 6 : 1 by weight, respectively. In other words, for the same quantity of carbon, there was twice as much hydrogen by weight in methane as in ethylene. Similarly, he found for the same weight of carbon, carbon dioxide contains twice as much oxygen as does carbon monoxide. After investigating other pairs of substances, Dalton formulated the **law of multiple proportions** about 1804. This law was tested by Berzelius in 1810 and may be stated thus: "If several compounds be formed, the fixed proportions in which two elements combine are in simple integral ratios to one another."

Law of Combining Weights. Richter, in his researches from 1792 to 1799, found that it was possible to assign to each element a fixed number, which in itself, or when multiplied by some whole number, represents the weight of the element that combines with other elements to form chemical compounds. This is called the **law of combining weights** (formerly known as the law of reciprocal proportions) and really includes the laws of definite and of multiple proportions. The work of Richter was extended by Dalton, Berzelius, Stas, and others.

By assigning oxygen a fixed weight value of 8 (grams) as a standard for comparison, then the weight of each of the other elements which combines with, or takes the place of, 8 parts by weight of oxygen can be determined. These weights are called **equivalent weights.** Originally hydrogen was taken as the standard, as it has the smallest equivalent, and was assigned a value of unity. In practice, the ratio **metal** : **oxygen** can usually be determined with greater ease and accuracy than the ratio **metal** : **hydrogen,** and therefore oxygen is now used as standard instead of hydrogen. Of course, any arbitrary number could be assigned to oxygen, but when 8 is employed, no element has an equivalent weight less than unity. Hydrogen, on the basis of 8 for oxygen, has an equivalent weight of 1.0078.

ATOMS AND MOLECULES

The structure of matter was an important topic of the ancient philosophers. The Greeks were divided into two schools: the school of Aristotle (384–322 B.C.) which taught that matter is infinitely divisible, and the school of Democritus (470–360 B.C.) which held that matter is finitely divisible; that is, composed of atoms (Greek *ἄτομος*, indivisible). This latter theory contained the germ of the modern theory of the structure of matter. Near the close of the seventeenth century Robert Boyle seems to have believed that chemical compounds are formed by the union of atoms. Sir Isaac Newton (1642–1727) believed that matter is made up of solid, hard, impenetrable, movable particles. John Dalton followed up these early speculations and at the beginning of the nineteenth century (about 1803) advanced his **atomic theory.** According to Dalton's theory every element is composed of minute, indivisible particles called atoms; atoms of the same element have the same weight and those of different elements have different weights; and compounds are formed by the union of atoms of different kinds in simple numerical proportions. This theory offered a rational explanation of the law of definite proportions. A few years later the Italian physicist, Avogadro (1811), made the distinction between **atoms** and **molecules** (Latin, a **little mass**). An atom, he said, is the smallest particle which can enter into chemical union; a molecule is the smallest portion of matter which can exist in the free state. In order to explain the uniform behavior of gases, Avogadro made the assumption that **under the same conditions of temperature and pressure, equal volumes of all gases contain the same number of molecules.** This is known as **Avogadro's hypothesis.** It has been tested thoroughly, both experimentally and mathematically, and is now one of the most useful laws of physics and of chemistry. There is much independent proof that atoms and molecules really do exist. In fact, much is now known about the structure of atoms and of molecules and so the atomic theory rests upon a firm foundation, although it has been modified somewhat to conform with newly discovered facts, such as the behavior of the radioactive elements and the existence of **isotopes** (see pages 14 and 256).

ATOMIC AND MOLECULAR WEIGHTS

Atomic Weights. Although equivalent weights are often used by chemists, a set of **relative weights** is much more frequently employed. These relative weights are called **atomic weights,** and they are either identical with, or are simple multiples of, the equivalent weights of the elements. A few equivalent weights and the corresponding atomic weights are given in the following table:

TABLE I

Element	Equivalent Weight	Atomic Weight
Oxygen (the standard)	8.0000	16.0000
Hydrogen	1.0078	1.0078
Chlorine	35.457	35.457
Carbon	3.00	12.00
Aluminum	8.99	26.97
Copper	31.785	63.57
Sodium	23.00	23.00

A complete table of the atomic weights of the elements will be found on page 10. These values of the atomic weights were published in 1936 by the International Committee on Atomic Weights.

Molecular Weights. The molecular weight of a substance is equal to the sum of the atomic weights of the elements which compose it. For example, the molecular weight of water, H_2O, is $(2 \times 1.0078) + 16.000 = 18.0156$; the molecular weight of sodium chloride, NaCl, is $23.00 + 35.457 = 58.457$; and so on.

It will be remembered that Avogadro's hypothesis (1811) states that, under the same conditions of temperature and pressure, equal volumes of different gases contain the same number of molecules. From this it follows that the molecular weights of gases are proportional to their densities. By taking oxygen as standard and assigning it a molecular weight of 32, as there are two atoms of oxygen in its molecule, we have,

$$\text{Density of any gas} : \text{Density of oxygen} = M : 32$$

where M is the molecular weight of the gas in question. For example, the densities of oxygen and of nitrogen under standard conditions of temperature and pressure are 1.4290 and 1.2507,

TABLE II

INTERNATIONAL ATOMIC WEIGHTS, 1936

Published by the *Journal of the American Chemical Society*

	Symbol	Atomic Number	Atomic Weight		Symbol	Atomic Number	Atomic Weight
Aluminum	Al	13	26.97	Molybdenum	Mo	42	96.0
Antimony	Sb	51	121.76	Neodymium	Nd	60	144.27
Argon	A	18	39.944	Neon	Ne	10	20.183
Arsenic	As	33	74.91	Nickel	Ni	28	58.69
Barium	Ba	56	137.36	Nitrogen	N	7	14.008
Beryllium	Be	4	9.02	Osmium	Os	76	191.5
Bismuth	Bi	83	209.00	Oxygen	O	8	16.0000
Boron	B	5	10.82	Palladium	Pd	46	106.7
Bromine	Br	35	79.916	Phosphorus	P	15	31.02
Cadmium	Cd	48	112.41	Platinum	Pt	78	195.23
Calcium	Ca	20	40.08	Potassium	K	19	39.096
Carbon	C	6	12.00	Praseodymium	Pr	59	140.92
Cerium	Ce	58	140.13	Protactinium	Pa	91	231
Cesium	Cs	55	132.91	Radium	Ra	88	226.05
Chlorine	Cl	17	35.457	Radon	Rn	86	222
Chromium	Cr	24	52.01	Rhenium	Re	75	186.31
Cobalt	Co	27	58.94	Rhodium	Rh	45	102.91
Columbium	Cb	41	92.91	Rubidium	Rb	37	85.44
Copper	Cu	29	63.57	Ruthenium	Ru	44	101.7
Dysprosium	Dy	66	162.46	Samarium	Sm	62	150.43
Erbium	Er	68	167.64	Scandium	Sc	21	45.10
Europium	Eu	63	152.0	Selenium	Se	34	78.96
Fluorine	F	9	19.00	Silicon	Si	14	28.06
Gadolinium	Gd	64	157.3	Silver	Ag	47	107.880
Gallium	Ga	31	69.72	Sodium	Na	11	22.997
Germanium	Ge	32	72.60	Strontium	Sr	38	87.63
Gold	Au	79	197.2	Sulfur	S	16	32.06
Hafnium	Hf	72	178.6	Tantalum	Ta	73	180.88
Helium	He	2	4.002	Tellurium	Te	52	127.61
Holmium	Ho	67	163.5	Terbium	Tb	65	159.2
Hydrogen	H	1	1.0078	Thallium	Tl	81	204.39
Indium	In	49	114.76	Thorium	Th	90	232.12
Iodine	I	53	126.92	Thulium	Tm	69	169.4
Iridium	Ir	77	193.1	Tin	Sn	50	118.70
Iron	Fe	26	55.84	Titanium	Ti	22	47.90
Krypton	Kr	36	83.7	Tungsten	W	74	184.0
Lanthanum	La	57	138.92	Uranium	U	92	238.14
Lead	Pb	82	207.22	Vanadium	V	23	50.95
Lithium	Li	3	6.940	Xenon	Xe	54	131.3
Lutechium	Lu	71	175.0	Ytterbium	Yb	70	173.04
Magnesium	Mg	12	24.32	Yttrium	Y	39	88.92
Manganese	Mn	25	54.93	Zinc	Zn	30	65.38
Mercury	Hg	80	200.61	Zirconium	Zr	40	91.22

respectively. Hence, the molecular weight of nitrogen may be calculated as follows:

$$1.2507 : 1.4290 = M : 32$$

$$M = 32 \times \frac{1.2507}{1.4290} = 28$$

Since the chemist uses the gram as unit of weight, 28 g. of nitrogen and 32 g. of oxygen are the respective **gram-molecular weights** of these gases. This weight is often called simply the **molar weight,** or **mol.** The volume occupied by one mol of all gases, at standard temperature (0° C.) and pressure (760 mm. of mercury), is approximately 22.4 liters and is called the **gram-molecular volume** or simply the **G.M.V.** The following table gives the weight (in grams) of one liter and the G.M.V. of a few of the more common gases at standard temperature and pressure (S.T.P.).

TABLE III

Gas	Weight of 1 Liter	G. M. V.
Hydrogen	0.0899	22.42
Ammonia	0.7708	22.09
Carbon monoxide	1.2500	22.40
Nitrogen	1.2507	22.40
Oxygen	1.4290	22.39
Hydrogen chloride	1.6410	22.22
Carbon dioxide	1.9766	22.26
Sulfur dioxide	2.9296	21.88
Chlorine	3.2200	22.02

To find the molecular weight of a gas or vapor it is only necessary to determine the weight of 22.4 liters of it, at S.T.P.; that is, multiply the weight of one liter of the gas or vapor, at S.T.P., by the constant 22.4. Of course it is not necessary actually to measure the gas at S.T.P. Any convenient temperature and pressure are chosen and then the volume is corrected to S.T.P. Moreover, it is not necessary to deal with a single molecule of each gas, since equal volumes of different gases contain the same number of molecules. Therefore, dealing with equal volumes of different gases is equivalent to dealing with an individual molecule of each. However, the number of molecules in 22.4 liters, at S.T.P., is known with a high degree of accuracy and is called **Avogadro's number** or **Avogadro's constant.** This number is represented by N and has a value of 6.06×10^{23} with an error probably not exceeding 0.1 per cent. This is Millikan's value, and it is in good agreement with values obtained by others using entirely different methods. Perrin determined N from Brownian movement observations, Planck from experimentally determined radiation constants, Rutherford from a measurement of the charge on the alpha particle from radium, and Rutherford and Boltwood by a direct count of alpha particles and a measurement of the resulting volume of helium.

The absolute weight of a single atom or molecule can be obtained by dividing the respective atomic or molecular weight by the Avogadro number. For example, the weight of an atom of hydrogen is $1.0078 \div 6.06 \times 10^{23} = 1.66 \times 10^{-24}$ g., and the weight of a molecule of hydrogen is $2.0156 \div 6.06 \times 10^{23} = 3.32 \times 10^{-24}$ g. Similarly, we calculate the weight of a single atom of oxygen to be 2.645×10^{-23} g. and the weight of a single oxygen molecule to be 5.29×10^{-23} g.

Cannizzaro's Method of Determining Atomic Weights. Although Avogadro enunciated his hypothesis in 1811, it was almost a half century later before the Italian chemist, Cannizzaro (1858), showed how it could be applied to the determination of the atomic weights of non-volatile elements. By preparing a large number of volatile compounds of each non-volatile element and then determining their **vapor densities** and percentage composition, the molecular weights of the compounds and in turn the atomic weights of the elements composing them can be determined. **The smallest weight in grams of an element found in the gram-molecular weight of any of its volatile compounds is taken as the atomic weight of the element.** In other words, we obtain the atomic weight expressed in grams by simply selecting the smallest weight of the element in the G.M.V., for an atom is defined as the smallest particle in a molecule. The atomic weight thus obtained is not an exact one, since Avogadro's hypothesis is only an approximation. However, the **equivalent weight** of an element can be determined with a high degree of accuracy, and hence the **exact atomic weight** can be obtained by multiplying the equivalent weight by the **valence. The valence of an element is equal to the number of hydrogen or chlorine atoms which one**

of its atoms can hold in combination or displace in a reaction. The approximate atomic weight obtained from vapor densities is close enough to establish the correct valence of the element.

Dulong and Petit's Method of Determining Atomic Weights. In 1819 Dulong and Petit, French physicists, made the important discovery that **the product of the atomic weight of a solid element and its specific heat is approximately constant.** This constant is called the **atomic heat,** and its present accepted value is 6.4. This is known as the **law of specific heats** and may be written:

$$\text{Atomic weight} \times \text{Specific heat} = 6.4$$

Hence,

$$\text{Atomic weight} = \frac{6.4}{\text{Specific heat}}$$

The specific and atomic heats of some of the solid elements are given in the following table:

TABLE IV

Element	Atomic Weight	Specific Heat	Atomic Heat
Lithium	6.940	0.9063	6.29
Sodium	22.997	0.2829	6.51
Potassium	39.10	0.166	6.5
Calcium	40.08	0.170	6.8
Iron	55.84	0.1189	6.64
Silver	107.880	0.0590	6.36
Tin	118.70	0.0551	6.55
Platinum	195.23	0.0323	6.31
Gold	197.2	0.0330	6.51
Mercury	200.61	0.032	6.4
Lead	207.22	0.0310	6.42
Uranium	238.14	0.0280	6.67

It is indeed remarkable that elements which differ so widely in atomic weight and other properties as do lithium and mercury should have almost identical atomic heats. The atomic heats at ordinary temperatures of a few of the elements are too low; for example, the atomic heats of beryllium (3.7), amorphous boron (2.8), crystalline carbon (1.7), and crystalline silicon (4.5) are much below 6.4. At higher temperatures the atomic heats of these elements approach the value 6.4. Thus the atomic heat of carbon (diamond) at 985° C. is 5.5 and that of silicon at 232° C. is 5.63.

Determination of Atomic Weights by Applying Mitscherlich's Law of Isomorphism. Mitscherlich in 1819 discovered that **substances which are similar in crystalline form and in chemical properties can usually be represented by similar formulas.** This is called the **law of isomorphism,** and it has been very useful in the determination or rectification of atomic weights. Thus, Mitscherlich observed that the phosphates and arsenates represented by the following pairs of formulas are isomorphous, and, hence, one set of formulas can be changed into the other merely by writing As instead of P:

$NaH_2PO_4 \cdot H_2O$ KH_2PO_4 $NH_4H_2PO_4$
$NaH_2AsO_4 \cdot H_2O$ KH_2AsO_4 $NH_4H_2AsO_4$

In these compounds 31 parts by weight of phosphorus are replaced by 75 parts by weight of arsenic. Hence, since 31 is the atomic weight of phosphorus, it follows that 75 must be the atomic weight of arsenic.

Isotopes. In 1815–1816 Prout, an English physician, announced an hypothesis that all the elements were made up of groups of hydrogen atoms only and that the atomic weights of the elements are exact multiplies of the atomic weight of hydrogen. This hypothesis was apparently untenable, as Berzelius (1779–1848) had made very careful atomic-weight determinations of most of the elements then known and the atomic weights of some of them were not even approximate multiples of that of hydrogen. So Prout's hypothesis fell into disrepute. In order to give the hypothesis a very critical test, Stas and Marignac about the middle of the nineteenth century each made many precise determinations of atomic weights and found some with fractional values. In fact the atomic weights of certain elements, for example chlorine 35.5, were not even approximate whole numbers. So Prout's hypothesis was discarded as being untenable. Moseley's discovery of **atomic numbers** in 1913 (see page 20) made Prout's hypothesis seem more plausible.

About twenty years ago, T. W. Richards of Harvard University discovered that lead from uranium minerals has an atomic weight only slightly above 206. About the same time, Soddy and Hyman, British physicists, found that lead from thorium minerals has an atomic weight slightly above 208. Ordinary lead has an atomic weight 207.22. Both Richards, and Soddy and Hyman took the greatest pains to purify all their materials and in making the atomic-weight determinations, so there is no doubt about the correctness of their results. Hence, it was definitely proved that atoms of the same element may have different atomic weights. Such atoms are called **isotopes.** The name was proposed by Soddy and is derived from the Greek ἴσος, **equal,** and τόπος, **place,** and means that these elements occupy the "same place" in the periodic classification. Ordinary chlorine is made up of two isotopes having atomic weights of 35 and 37 and mixed in such proportion to give ordinary chlorine an atomic weight of 35.46. F. W. Aston, an English physicist, has determined the atomic masses of a large number of isotopes of the elements by means of his **mass spectrograph.** Isotopes of a given element have the same chemical and physical properties but differ from each other in weight. This makes it necessary to redefine an **element** as **a substance in which all the atoms have the same atomic number.** According to Aston, an element is "a substance with definite chemical and spectrographic properties, which may or may not be a mixture of isotopes."

Many atomic weights are not exactly whole numbers because they represent elements which are isotopic mixtures. The masses of isotopes have been found by Aston to be almost exactly whole numbers, within the limits of accuracy of his method. So Prout's hypothesis (1815) has some foundation after all. Indeed, exactly one hundred years later (1915), Harkins proposed a theory which is very similar to Prout's; namely, that the elements are made up of hydrogen and helium atoms. A similar theory was advanced by Rutherford about this same time. In fact, Rutherford (1922) has succeeded in ejecting **hydrogen ions (protons,** see page 16) **from nitrogen** and several other light elements by bombarding their atoms with alpha particles, i.e., positively charged helium atoms (He^{++}). Now the weight (mass) of a hydrogen atom is 1.0078. The weight (mass) of a helium atom is 4.002. Hence, if a helium atom is composed of four hydrogen atoms its weight should be $1.0078 \times 4 = 4.0312$. So there is a loss in weight (mass) equal to 0.0292. Rutherford and Harkins suggest that when 4 hydrogen atoms come together to form an atom of helium, the excess matter or mass, namely, 0.0292, appears as energy.

At present there is no real distinction between matter and energy. Matter is potential energy, and energy is potential matter.

Transmutation of atoms has been accomplished with most of the lighter elements. The disintegration of atoms is frequently also synthesis. Thus, $He^4 + N^{14} = 0^{17} + H^1 +$ Energy. Recently "artificial" or "induced" radio-sodium (atomic weight 24) has been produced.

ELECTRONS, PROTONS, AND QUANTA

Electrons and Protons. Until the beginning of the twentieth century atoms were believed to be the ultimate units of elements. It was thought that atoms could not be resolved into smaller particles. However, it has now been proved definitely that an atom is composed of a dense nucleus of positive electricity surrounded by particles of negative electricity. The unit of positive electricity is the hydrogen nucleus and is called a **proton,** from the Greek word πρῶτον meaning **first** or **primary substance.** The unit of negative electricity is called an **electron.** The mass of a proton is 1845 times the mass of an electron, and its volume is correspondingly **smaller.** Millikan's value for the electronic charge is 4.774×10^{-10} electrostatic unit. The proton has the same charge as the electron, but of opposite sign. The removal of electrons from atoms produces positive ions, and the gaining of extra electrons by atoms produces negative ions.

Quanta. When atoms absorb energy, electrons are displaced; and when they return to their normal position, light is emitted. Light, or any form of radiant energy, is composed of small units of energy called **quanta.** The energy in a quantum varies with the frequency according to the fundamental equation,

$$\epsilon = h\nu$$

where ϵ is the energy, ν is the frequency of the radiation, and h is Planck's universal constant which has a value of 6.55×10^{-27} erg-second. This equation is the basis of the quantum theory, which has been a powerful tool in the newer physics and theoretical chemistry.

PROBLEMS

1. What is the molecular weight of each of the following compounds: (*a*) silver chloride, (*b*) lead chloride, (*c*) mercuric sulfide, (*d*) arsenic sulfide, and (*e*) stannous sulfide?

2. Find the molecular weight of (*a*) aluminum hydroxide, (*b*) sodium aluminate, (*c*) tricalcium phosphate, (*d*) magnesium ammonium phosphate, and (*e*) cupric sulfate pentahydrate.

3. The density of hydrogen is 0.0899 at 0° C. and 760 mm. of mercury pressure. Under the same conditions, sulfur dioxide has a density of 2.9296. Calculate the molecular weight of sulfur dioxide.

4. Calculate the density of pure, dry air at S.T.P. Air has the following percentage composition by volume: nitrogen, 78.06; oxygen, 21.00; argon (plus the other inert gases), 0.94.

5. (*a*) The G.M.V. of ammonia is 22.09 at S.T.P. What is its density? (*b*) Calculate the density of hydrogen chloride.

6. (*a*) One liter of carbon dioxide weighs 1.9766 g. at 0° C. and 760 mm. What is its molecular weight? (*b*) Calculate the weight of one liter of each of the following gases: hydrogen sulfide, carbon monoxide, and helium.

7. Calculate the weights of single atoms of nitrogen, fluorine, chlorine, helium, neon, and argon, respectively.

8. Calculate the weights of single molecules of the following gases: ammonia, hydrogen chloride, carbon monoxide, carbon dioxide, nitrogen, and chlorine.

9. (*a*) The specific heat of silver is 0.0590. Calculate the atomic heat of silver. (*b*) The specific heat of platinum is 0.0323. What is the atomic weight of platinum?

10. From specific heat data on page 13, calculate the approximate atomic weights of the following metals: sodium, calcium, iron, gold, mercury, and lead.

CHAPTER III

ELEMENTS, COMPOUNDS, AND MIXTURES

CLASSIFICATION OF THE ELEMENTS

For a long time the elements have been classed as metals or base-forming elements, and as non-metals or acid-forming elements. This is an arbitrary division, for it is not possible to make a sharp distinction. Certain elements (e.g., arsenic and antimony) possess both metallic and non-metallic properties, that is, they are both basic and acidic in character. Such elements are called **metalloids, or amphoteric elements.** Notwithstanding the fact that elements cannot be grouped into two sharply defined classes, the classification as metals and non-metals is a convenient one. Metals have a "metallic" luster, they are malleable, ductile, and are good conductors of electricity. Non-metals, on the other hand, do not as a rule have these characteristics. Moreover, they generally have lower densities, lower melting-points, and lower boiling-points than the metals. The metals may be divided into **light metals** and **heavy metals,** the latter having densities greater than five times that of water.

Döbereiner's Triads. During the years 1816 to 1829 Döbereiner called attention to the fact that certain groups of three elements each (e.g., Cl 35.5, Br 79.9, I 126.9) could be selected such that the three elements were chemically similar and the second element had an atomic weight approximately the arithmetical mean of those of the first and third members of the group. Furthermore, he observed that certain closely related elements in groups of three have atomic weights which are almost the same (e.g., Fe 55.8, Co 58.9, Ni 58.7). These groups of three elements became known as **triads** and were the forerunner of the periodic law, which will be discussed subsequently.

De Chancourtois' Helix. In 1862 de Chancourtois arranged the elements in the order of their atomic weights, on a right-circular cylinder at a constant angle of 45°. One-sixteenth of a complete revolution of the cylinder was taken as a unit of measure. He pointed out that elements with similar properties fall on vertical lines parallel to the generatrix. A modern helical arrangement of the elements was published by two American chemists, Harkins and Hall, in 1916.

Newlands' Law of Octaves. About 1864 Newlands, of England, discovered that, when the elements are arranged in the order of their atomic weights, the eighth element has properties very similar to the first, "a kind of repetition of the first, like the eighth note of an octave in music." He called this striking relationship the **law of octaves.** This generalization was the immediate forerunner of the periodic law.

The Periodic Law. When the elements are arranged according to their atomic weights, they fall into eight periodic groups according to their properties. This arrangement of the elements is known as the periodic table or the periodic system and was developed independently and almost simultaneously by Mendeléeff (1869), of Russia, and Lothar Meyer, of Germany. A few years earlier (1863–1864), Newlands had published his classical papers on his law of octaves. At the time Mendeléeff published his first periodic table (1871) only about sixty-five elements were known, but he boldly stated that other elements would be discovered to fill in the vacant places in his table and even went so far as to predict the properties of some of them. A few years later, when several of these elements were discovered, their properties and those of certain of their compounds were in striking agreement with the predictions of Mendeleéff. The grouping of elements according to their atomic weights is expressed by the **periodic law: The properties of the elements and their compounds are periodic functions of the atomic weights of the elements.** The periodic system has greatly simplified the study of the elements and their compounds, has enabled the prediction of new elements, has aided in the estimation and correction of atomic weights, and has suggested problems for investigation. This system, however, is not perfect. For instance, hydrogen is without a place in the groups of the elements, and there are three exceptions to the arrangement of the elements in the order of increasing atomic weights; namely, argon (at. wt. 39.9) precedes potassium (at. wt. 39.1), cobalt (at. wt. 58.94) precedes nickel (at. wt. 58.69), and tellurium (at. wt. 127.61) precedes iodine (at. wt. 126.92). Notwithstanding these imperfections and several others, undoubtedly some fundamental relationship is represented in the periodic arrangement of the elements. If the atomic weights of the elements are plotted as abscissas and various physical properties as ordinates, wave-shaped curves are obtained that are quite similar. For example, the following properties may be plotted: atomic volumes, reciprocals of the absolute melting-points, coefficients of expansion, and the compressibilities of the atoms.

Moseley's Atomic Numbers. When cathode rays (streams of electrons) emanating from the cathode of a vacuum tube are suddenly stopped by striking a solid target placed at the anode, radiation from the anode occurs; that is, X-rays are produced. In 1913, using different elements, from aluminum to gold, as targets, Moseley, one of the most brilliant of the younger British physicists, obtained X-rays of slightly different wave-lengths. He observed that, the higher the atomic weight of the element, the shorter the wave-length of the X-rays. He arranged the elements in the order of increasing frequency of the characteristic X-rays which they emit and numbered them. These numbers he called **atomic numbers** (see Table II). Other investigators have confirmed and added to the work of Moseley. The elements thus numbered, starting with hydrogen as 1, then helium 2, etc., to uranium 92, are arranged in the same order as that of increasing atomic weights, except in the three cases mentioned above where the order is reversed. Thus at the age of twenty-seven, Moseley had completed one of the most significant pieces of research of the last half century. Unfortunately the World War cut short his brilliant career, and while in the trenches at Gallipoli on August 10, 1915, young Moseley was instantly killed by a Turkish bullet. His will, made while he was in active service, bequeathed all his apparatus and much of his estate to the Royal Society.

New Elements. As previously mentioned there are ninety known chemical elements. The arrangement by atomic weights and by atomic numbers indicates that there should exist ninety-two elements. An inspection of the periodic table shows that elements number 85 and number 87 are missing. Recently Allison[1] and his co-workers have announced the discovery of elements 85 and 87. However, since his magneto-optic method of analysis

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[1] Allison and Murphy, *Phys. Rev.*, **35**, 285 (1930); Allison, Murphy, Bishop, and Sommer, *ibid.*, **37**, 1178–80 (1931).

has not been completely verified, the discovery of the last two elements is in doubt, and hence there are two gaps in the periodic table.

The question naturally arises, is there reason to expect the existence of elements with atomic weights higher than uranium, element 92? All attempts to demonstrate the existence of an element having an atomic weight greater than that of uranium have been unsuccessful. The heavier elements are **radioactive**; that is, they are undergoing spontaneous and constant disintegration, thus forming elements of lower atomic weights. It is reasonable to assume that any elements having atomic weights greater than that of uranium would be very radioactive, and hence it seems probable that if any ever existed they have long since disintegrated into lighter elements. If this hypothesis is true, then we need not expect to discover any elements beyond uranium, element 92.[2]

COMPOUNDS AND MIXTURES

Compounds are pure substances and may be decomposed into, or formed from, simpler substances. They are homogeneous and have a definite composition by weight. Mixtures are heterogeneous and are composed of two or more independent components which are variable in amount. The components of a mixture may often be separated by mechanical means. The term constituent refers to the individual elements joined by chemical union in compounds. More than 275,000 different compounds are known (exclusive of simple derivatives). About 250,000 of these are carbon compounds and 25,000 inorganic compounds. The majority of the compounds have been synthesized in the laboratory; only a comparatively small number exist in nature.

COMPOUNDS AND THEIR FORMULAS

Structural Formulas. If the valence of atoms be represented by bonds or lines, then formulas for compounds may be written so as to represent the manner in which the atoms are joined in the molecule. Such formulas are called **structural formulas,** also

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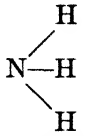
[2] It has recently (1935) been announced that Dr. A. V. Grosse of the University of Chicago has obtained the first definite indication of the existence of a super-heavy element beyond 92 in the periodic table.

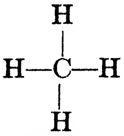
graphic or **constitutional formulas.** In such formulas each atom has as many bonds or lines as it has valences. The following are examples:

H—Cl
Hydrogen chloride

H—O—H
Water

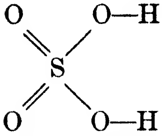


Ammonia

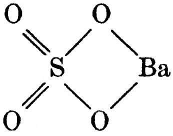


$$\begin{array}{ccccc} & & H & & \\ & & | & & \\ H & - & C & - & H \\ & & | & & \\ & & H & & \end{array}$$

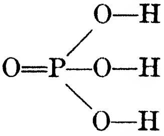
Methane



Sulfuric acid

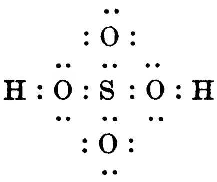


Barium sulfate

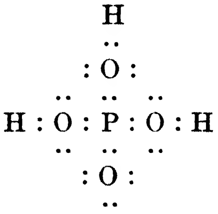


Phosphoric acid

Electronic Formulas. According to the electron theory of valence, the electrons in the outer shell of an atom are the valence electrons. If we represent the nucleus of an atom by its ordinary symbol and the surrounding outer electrons by dots, then we may write structural or graphic formulas in which the valence bonds or lines are replaced by dots. Such formulas are called **electronic formulas.** Thus we may write the electronic formulas for H_2SO_4 and H_3PO_4:



$$\begin{array}{ccccccccc} & & & & \cdot\cdot & & & & \\ & & & : & O & : & & & \\ & & \cdot\cdot & & \cdot\cdot & & \cdot\cdot & & \\ H & : & O & : & S & : & O & : & H \\ & & \cdot\cdot & & \cdot\cdot & & \cdot\cdot & & \\ & & & : & O & : & & & \\ & & & & \cdot\cdot & & & & \end{array}$$

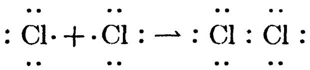


$$\begin{array}{ccccccccc} & & & & H & & & & \\ & & & & \cdot\cdot & & & & \\ & & & : & O & : & & & \\ & & \cdot\cdot & & \cdot\cdot & & \cdot\cdot & & \\ H & : & O & : & P & : & O & : & H \\ & & \cdot\cdot & & \cdot\cdot & & \cdot\cdot & & \\ & & & : & O & : & & & \\ & & & & \cdot\cdot & & & & \end{array}$$

Polar, Non-Polar, and Coordinate Compounds. Three types of linkages are recognized in molecules, namely: (1) polar or ionizable, (2) non-polar or non-ionizable, and (3) coordinate or secondary linkages.

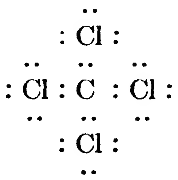
Polar compounds are composed of oppositely charged ions held together by electrostatic attraction. This type of linkage or valence is called **electrovalence.** In the formation of polar compounds, one or more electrons is considered as being transferred from one atom to another, for example, Na^+Cl^-, the electronic formula for which is $Na:\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}:$. Compounds of this type are therefore potentially ionized, but the ions can be separated only by a medium which has a high dielectric constant (e.g., water).

Non-polar compounds are formed when atoms unite without a transfer of electrons. The union is said to be accomplished by a **sharing** of electrons as, for example, in the chlorine molecule:



$$:\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}\cdot + \cdot\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}: \rightarrow :\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}:$$

This type of linkage is sometimes called covalent or non-ionizable linkage and is especially common in carbon compounds, for example, carbon tetrachloride, CCl_4:



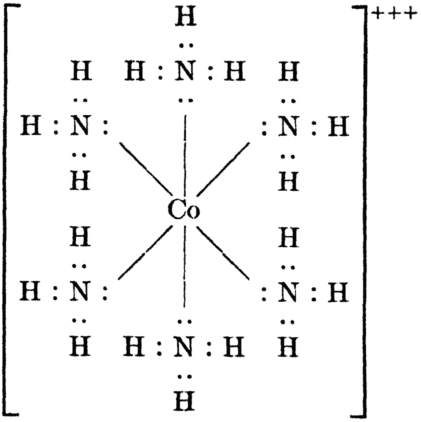
$$\begin{array}{c} :\overset{\cdot\cdot}{Cl}: \\ :\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{C}}\ :\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}: \\ :\underset{\cdot\cdot}{Cl}: \end{array}$$

It should be emphasized that there is no sharp distinction between polar and non-polar compounds; the difference is one of degree and not of kind.

Coordinate compounds are those formed by "secondary" or "residual" valences and are discussed in some detail on pages 169–183. In such compounds, Werner calls ordinary valence "primary" and the residual attraction "secondary" valence. The number of groups (atoms, molecules, ions, or radicals) joined to the central atom, forming a non-ionizable or very slightly ionizable "nucleus," is called the **coordination number.**

According to Werner each element has a **maximum** coordination number. For most metals this number is 6; for non-metals it is 4. In general, as the electrode potential of the elements decreases (see page 226), their tendency to form complexes increases. Thus gold, platinum, silver, copper, nickel, cobalt, iron, etc., form many complex compounds readily. On the other hand, the alkali elements show very little tendency to form complex compounds.

The electronic formula for the cobalt ammonia complex ion, $[Co(NH_3)_6]^{+++}$, may be written thus:



CHAPTER IV

THE CHANGES OF MATTER. MASS, WEIGHT, AND DENSITY

Matter is continuously undergoing changes; for example, iron rusts, coal burns, water freezes or boils; in fact all the many processes of life itself are undergoing changes. Often the changes which take place do not involve a transformation of matter into new substances. Such changes are physical only, as in the boiling of a liquid or the melting of a solid. When a change in composition takes place, it is a chemical change, as for example, the rusting of iron or the burning of coal. The various ways in which chemical changes take place may be grouped under four types of reactions as follows:

1. Combination. An example of this type of chemical change is the combination of iron and sulfur to form ferrous sulfide when an intimate mixture of them is heated to a red heat in a test tube. The change is represented by the following equation:

$$\underset{1\text{ g.}}{\text{Iron}} + \underset{0.57\text{ g.}}{\text{Sulfur}} \rightarrow \underset{1.57\text{ g.}}{\text{Ferrous sulfide}}$$

2. Decomposition. When mercuric oxide is heated in a test tube it decomposes into its constituent elements, mercury and oxygen. The change is expressed as follows:

$$\underset{1\text{ g.}}{\text{Mercuric oxide}} \rightarrow \underset{0.93\text{ g.}}{\text{Mercury}} + \underset{0.07\text{ g.}}{\text{Oxygen}}$$

Decomposition is the reverse of combination.

3. Displacement. A third type of chemical change is known as displacement. In this process one element displaces another from its compounds. This is illustrated in the displacement of copper from copper sulfate (blue vitriol) by iron. If an iron rod is dipped into an aqueous solution of copper sulfate, copper is plated out and an equivalent amount of iron dissolves:

$$\text{Copper sulfate} + \text{Iron} \rightarrow \text{Iron sulfate} + \text{Copper} \downarrow$$

4. Double Decomposition. This very common type of chemical change is the result of the interaction of two compounds to form two other compounds. For example, if aqueous solutions of sodium chloride (common salt) and silver nitrate are mixed, the parts into which they split unite to form silver chloride (insoluble) and sodium nitrate:

$$\text{Sodium chloride} + \text{Silver nitrate} \rightarrow \text{Silver chloride} \downarrow + \text{Sodium nitrate}$$

The precipitate of silver chloride may be filtered off and the sodium nitrate obtained by evaporating the filtrate to dryness.

Any chemical change in matter is called a **chemical reaction,** or **action,** or **interaction.** Such changes are always accompanied either by the consumption or the production of energy, such as heat, light, and electricity.

MASS, WEIGHT, AND DENSITY

Mass is a definite quantity of matter and is constant; that is, it is independent of its position with respect to other bodies. The **weight** of a substance depends upon its position in relation to the center of the attracting body, the earth.

$$\text{Weight} = \text{Mass} \times \text{Acceleration due to gravity, or } W = Mg$$

Since mass and weight are always directly proportional to each other, the two terms may be used interchangeably at any particular place. The **unit of mass** is the **gram,** which is the thousandth part of the standard mass of metal (platinum-iridium alloy) called the **kilogram.** The international standard of mass is kept at the International Bureau of Weights and Measures, near Paris. The **density** of a substance is the ratio of its mass to its volume, that is, mass per unit volume. $\text{Density} = \dfrac{\text{Mass}}{\text{Volume}}$, where mass is expressed in grams and volume in cubic centimeters. Water has its maximum density, 1, at 4° C.; i.e., one cubic centimeter of water at 4° C. weighs one gram. The density of gold is 19.32; i.e., one cubic centimeter of gold weighs 19.32 g.

THE CHEMICAL BALANCE

The chemical balance is an instrument for measuring the relative weights or masses of substances. No other instrument has contributed to the progress of chemistry as has the chemical balance, more commonly referred to as the analytical balance. The classical work of Lavoisier during the latter part of the eighteenth century was based upon the use of the balance.

With the introduction of the balance, chemistry became an exact science. Lord Kelvin once said, " When you can measure what you are speaking about and express it in numbers, you know something about it, and when you cannot measure it, when you cannot express it in numbers, your knowledge is of a meagre and unsatisfactory kind. It may be the beginning of knowledge, but you have scarcely in your thought advanced to the stage of a science."

PROBLEMS

1. (*a*) What weight of ferrous sulfide can be made by heating to a red heat an intimate mixture of 10 g. of sulfur and an excess of iron powder? (*b*) If 25 g. of iron were used, how much iron will remain uncombined?

Ans. (*a*) 27.4 g.
(*b*) 7.6 g.

2. (*a*) How many grams of hydrogen sulfide can be obtained by the action of an acid on 100 g. of ferrous sulfide? (*b*) What weight of cupric sulfide will the hydrogen sulfide obtained in (*a*) precipitate when allowed to react with an aqueous solution of a cupric salt? (Assume that none of the hydrogen sulfide escapes from the reaction vessel.)

Ans. (*a*) 38.8 g.
(*b*) 108.8 g.

3. (*a*) What weights of calcium oxide and carbon dioxide, respectively, are produced by the ignition of 1 kg. of calcium carbonate? (*b*) How much calcium hydroxide can be prepared from the lime obtained in (*a*)?

Ans. (*a*) 0.56 kg., 0.44 kg.
(*b*) 0.74 kg.

4. A clean iron rod is dipped into a solution of copper sulfate. After five minutes the rod is withdrawn and the solution analyzed at once (to prevent oxidation) for ferrous sulfate. If 0.25 g. of ferrous sulfate was found, (*a*) how much iron dissolved and (*b*) what weight of metallic copper was plated out?

Ans. (*a*) 0.092 g.
(*b*) 0.105 g.

5. (*a*) How much silver chloride is formed by the addition of 0.5 g. of ammonium chloride to a solution containing 10 g. of silver nitrate? (*b*) How

much ammonium nitrate was produced? (*c*) What weight of silver nitrate remained?

Ans. (*a*) 1.34 g.
(*b*) 0.75 g.
(*c*) 8.41 g.

6. (*a*) How many milligrams of lead and of chlorine, respectively, are contained in 0.100 g. of lead chloride? (*b*) How many milligrams of bismuth in 0.010 g. of bismuth sulfide?

Ans. (*a*) 74.5 mg., 25.5 mg.
(*b*) 8.1 mg.

7. (*a*) What weight of NH_3 is required to precipitate 100 mg. of aluminum as aluminum hydroxide? (*b*) What volume would this amount of ammonia gas occupy at S.T.P.?

Ans. (*a*) 189 mg.
(*b*) 0.25 l.

8. (*a*) How many cubic centimeters of carbon dioxide can be obtained at S.T.P. by the action of an excess of an acid upon 1 g. of calcite? (*b*) What weight of barium would this amount of carbon dioxide precipitate?

Ans. (*a*) 224 cc.
(*b*) 1.37 g.

9. (*a*) A solution contains 25 mg. of each of the following sulfates: copper, bismuth, cadmium, and mercury (ic). Calculate the amounts of each sulfide formed when the solution is saturated with hydrogen sulfide. (*b*) What was the total amount of sulfuric acid produced in (*a*)?

Ans. (*a*) 15.0 mg., 18.2 mg., 17.3 mg., 19.6 mg.
(*b*) 45.9 mg.

10. (*a*) How many milligrams of ammonium carbonate are required to precipitate 100 mg. of each of the following: calcium, strontium, and barium? (*b*) An excess of sodium hydroxide is added to a solution containing 1 g. of ammonium sulfate and the solution boiled to expel the ammonia gas. What was the weight (in milligrams) of the gas, and what volume (in cubic centimeters) would it occupy at N.T.P.?

Ans. (*a*) 240 mg., 110 mg., 70 mg.
(*b*) 258 mg., 340 cc.

CHAPTER V

OXIDATION-REDUCTION REACTIONS

Oxidation-reduction reactions involve valence changes; that is to say, some atom or ion undergoes an increase in valence and simultaneously some other atom or ion undergoes a decrease in valence. This change in valence differentiates oxidation-reduction reactions from all other types of reactions. Oxidation may be defined as a chemical change in which electrons are lost by an atom or ion. Reduction is the reverse process of oxidation; namely, electrons are gained by an atom or ion. The two processes take place simultaneously. In other words, in every oxidation-reduction reaction there is a transfer of one or more electrons, the reducing agent being oxidized and the oxidizing agent reduced. In order for a substance to function as a reducing agent (**reductant**), it must be capable of giving up one or more electrons; and in order to act as an oxidizing agent (**oxidant**), it must be able to take up one or more electrons. Hence, an oxidizing agent is not limited to substances containing oxygen, nor is a reducing agent limited to substances containing hydrogen. Moreover, certain substances, for example HNO_2, may act either as an oxidizing agent or as a reducing agent, depending upon whether it acts under conditions which permit it to lose electrons or to gain electrons.

BALANCING OXIDATION-REDUCTION EQUATIONS

There are two methods of balancing oxidation-reduction equations: (1) the " valence change " method and (2) the " ion-electron" method. The former is older and is based upon valence changes; the latter is based essentially upon electrochemical considerations. An excellent presentation of these methods is given by Jette and La Mer,[1] and the discussion which follows is based upon

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[1] Jette and La Mer, *J. Chem. Education,* **4**, 1021–30 and 1158–67 (1927).

their papers. These authors point out that "due to the limitations of our present knowledge, it is convenient to resolve this large group of reactions into two smaller groups": (1) **non-ionic** reactions, i.e., those which take place in the dry state between solids or between gases; and (2) **ionic** reactions, i.e., those which take place in aqueous solution between dissolved substances. That such a division is necessary, at least for the present, is clearly shown in the following paragraph.

> There is a large mass of evidence to show that reactions taking place in aqueous solution are the result of interactions between substances in the ionized state and further, in the case of strong electrolytes, modern theory teaches that the un-ionized form is entirely absent or, if it exists at all, only in exceedingly small concentrations. For the strong electrolytes the ions may be treated as the only important factors. In the other group of reactions, conclusive evidence that the interactions are only between ions is lacking, especially in reactions between gases. Molten salts such as NaCl and KNO_3 possess high electrical conductivity which indicates the presence of a considerable number of free ions. Solid salts also have properties which demonstrate that they are built up of ions rather than molecules. But for other solid substances as well as liquids and gases, the ionic nature of their interactions has not been demonstrated in nearly so conclusive a fashion as for the reactions taking place between dissolved salts. It is usually preferable to consider the molecular substances as the units in these cases. Any such classification of reactions is, of course, entirely arbitrary but none the less useful.

The Valence-Change Method. This method of balancing oxidation-reduction equations is here applied to non-ionic reactions and is as follows:

1. Determine the numerical change in the valence of the element undergoing reduction (the oxidizing agent). Do the same for the element undergoing oxidation (the reducing agent).
2. Make the numerical change of valence of each of these, the numerical coefficient of the other.
3. Since the principle underlying this method is, of course, that every oxidation involves a loss of electrons (increase of positive charge) and every reduction a gain of electrons, in the final equations the two changes in the number of electrons must exactly counter-balance in order to preserve electrical neutrality. Take the reaction between molten KNO_3 and free carbon as an example:

$KNO_3 \overset{2}{+} C \rightarrow KNO_2 + CO_2$ (Skeleton equation)

$2(N^{+5} + \underset{4}{2e} \rightarrow N^{+3})$ (Equation for oxidizing agent)

$C^\circ - 4e \rightarrow C^{+4}$ (Equation for reducing agent)

$2N^{+5} + C^\circ + 4e - 4e \rightarrow 2N^{+3} + C^{+4}$ (Valence-change equation)

$2KNO_3 + C \rightarrow 2KNO_2 + CO_2$ (Final molecular equation)

Although this method often gives the correct equation when applied to reactions taking place in aqueous solution, before it can be used it must be possible to select the particular atoms undergoing oxidation and reduction. This is not always a simple matter, and, moreover, the influence of such important factors as acidity and alkalinity, the presence of other ions, etc., is usually obscured when the valence-change method is applied to reactions in aqueous solutions. These difficulties are avoided and a greater insight into the nature of these reactions is gained by using the ion-electron method which follows.

The Ion-Electron Method. This method of balancing oxidation-reduction equations can be applied only to ionic reactions. Such reactions are frequently so complex that it is impossible to balance their equations "by inspection" or "by trial and error." But by following the rules proposed by Jette and La Mer, the balancing of oxidation-reduction equations for reactions taking place in solution is very much simplified. The interaction between $K_2Cr_2O_7$, NaI, and H_2SO_4 will be taken as an illustration.

Rule 1. Ascertain the products of the reaction. Without this knowledge it is impossible to balance the equation.

In the case of $K_2Cr_2O_7$, NaI, and H_2SO_4, the **main** products are Cr^{+++} ion and I_2. The consumption or production of H^+ ion will be taken care of by a correct application of the rules.

$$\underset{\text{Orange-red}}{Cr_2O_7^{=}} \rightarrow \underset{\text{Green}}{Cr^{+++}}$$

$$\underset{\text{Colorless}}{2I^-} \rightarrow \underset{\text{Brown}}{I^\circ_2}$$

These changes are experimental facts and may actually be observed.

Rule 2. Set up a partial equation for the oxidizing agent. To do this, it will be necessary to dispose of seven oxygen atoms. Always when the oxidizing ion contains more atoms of oxygen than its reduction product, H_2O is formed. Thus to balance this partial equation **chemically,** we write

$$Cr_2O_7^{=} + 14H^{+} \rightarrow 2Cr^{+++} + 7H_2O \qquad (1)$$

The decrease in H^+ ion concentration can be shown experimentally.

Rule 3. Set up a partial equation for the reducing agent in the same way. In the present case

$$2I^{-} \rightarrow I^{\circ}_2 \qquad (2)$$

Rule 4. Balance each of the partial equations **electrically.** In the first equation there are 14 positive and 2 negative charges on the left, making a net of 12 positive; and on the right there are 6 positives. In order to equalize the charges on the two sides of the equation, 6 electrons (i.e., 6 negative charges) are added on the left side. The second equation is electrically balanced by subtracting 2 electrons from its left side. The two electrically balanced partial equations are:

$$Cr_2O_7^{=} + 14H^{+} + 6e \rightarrow 2Cr^{+++} + 7H_2O$$

$$2I^{-} - 2e \rightarrow I^{\circ}_2$$

Rule 5. Multiply each partial equation by a factor so that when the two are added the electrons just compensate each other. In this example, it is only necessary to multiply the second partial equation by 3.

$$6I^{-} - 6e \rightarrow 3I^{\circ}_2$$

Rule 6. Now add the two partials. The result is the final **ionic equation** for the reaction,

$$Cr_2O_7^{=} + 14H^{+} + 6I^{-} \rightleftharpoons 2Cr^{+++} + 7H_2O + 3I^{\circ}_2$$

In some cases it will be possible to simplify the equation by canceling out certain substances which appear on both sides of the equation.

If desired, the molecular form of the equation may easily be written by adding the non-essential ions to the ionic equation. Any positive ion may be used for forming salts of $Cr_2O_7^{=}$ ion and

I^- ion, and any negative ion for forming the acid molecule. Since in the above example K^+, Na^+, and $SO_4^{=}$ are the non-essential ions, these will now be added to the ionic equation. The balanced molecular equation is thus obtained.

$$K_2Cr_2O_7 + 7H_2SO_4 + 6NaI$$
$$\rightleftharpoons Cr_2(SO_4)_3 + K_2SO_4 + 3Na_2SO_4 + 7H_2O + 3I_2$$

PROBLEMS

OXIDATION-REDUCTION EQUATIONS

1. What is the valence of the underscored element in each of the following formulas? $\underline{Mn}O_4^-$, $\underline{Cr}_2O_7^{=}$, $H\underline{N}O_3$, $\underline{Pb}O_2$, $Na_3\underline{As}O_3$, $\underline{Fe}SO_4$, $Na\underline{O}\underline{Cl}$, $\underline{Br}_2$, $K\underline{I}$, $H_2\underline{S}$.

7 +1 0

2. State which ions and compounds of question 1 are oxidizing agents under usual conditions and which are reducing agents.

3. State which of the following compounds are oxidizing agents and which are reducing agents: H_2S, $SnCl_4$, $FeSO_4$, HNO_3, $K_2Cr_2O_7$, $SnCl_2$, $HgCl_2$, $KMnO_4$, $FeCl_3$, and H_2SO_3.

4. Balance the following oxidation-reduction equations by the valence change method.

(1) $FeCl_2 + Cl_2 \rightleftharpoons FeCl_3$
(2) $CuSO_4 + KI \rightleftharpoons Cu_2I_2 + K_2SO_4 + I^\circ$
(3) $HCl + HNO_3 \rightleftharpoons H_2O + NOCl + Cl^\circ$
(4) $(NH_4)_2Cr_2O_7 \overset{\text{Heat}}{\rightleftharpoons} Cr_2O_3 + N^\circ + H_2O$
(5) $HNO_2 \rightleftharpoons HNO_3 + NO + H_2O$
(6) $NH_4NO_3 \overset{\text{Heat}}{\rightleftharpoons} N_2O + H_2O$
(7) $Cu^\circ + H_2SO_4 \rightleftharpoons CuSO_4 + SO_2 + H_2O$
(8) $Hg_2Cl_2 + NH_3 \rightleftharpoons Hg(NH_2)Cl + Hg + NH_4Cl$
(9) $Na_2S_2O_3 + I^\circ \rightleftharpoons Na_2S_2O_6 + NaI$
(10) $FeSO_4 + Ce(SO_4)_2 \underset{\text{solution}}{\overset{\text{In acid}}{\rightleftharpoons}} Fe_2(SO_4)_3 + Ce_2(SO_4)_3$

5. Write the balanced ionic equations for the following oxidation-reduction reactions, using the ion-electron method:

(11) $SbCl_5 + KI \rightleftharpoons SbCl_3 + KCl + I^\circ$
(12) $H_2S + I \rightleftharpoons HI + S^\circ$
(13) $CdS + I + HCl \rightleftharpoons CdCl_2 + HI + S^\circ$
(14) $CaC_2O_4 + KMnO_4 + H_2SO_4 \rightleftharpoons CaSO_4 + K_2SO_4 + MnSO_4 + H_2O + CO_2$
(15) $Na_2S_2O_3 + I_2 \rightleftharpoons Na_2S_4O_6 + NaI$
(16) $CaOCl_2 + HCl \rightleftharpoons CaCl_2 + H_2O + Cl^\circ$
(17) $FeCl_2 + K_2Cr_2O_7 + HCl \rightleftharpoons FeCl_3 + KCl + CrCl_3 + H_2O$
(18) $CuSO_4 + KI \rightleftharpoons Cu_2I_2 + K_2SO_4 + I^\circ$
(19) $KIO_3 + KI + HCl \rightleftharpoons KCl + H_2O + I^\circ$

(20) $KI + KMnO_4 + H_2SO_4 \rightleftharpoons K_2SO_4 + MnSO_4 + H_2O + I^\circ$
(21) $H_2S + HNO_3 \rightleftharpoons NO + H_2O + S^\circ$
(22) $FeCl_2 + Cl_2 \rightleftharpoons FeCl_3$
(23) $KI + Cl_2 \rightleftharpoons KCl + I^\circ$
(24) $HNO_2 \rightleftharpoons HNO_3 + NO + H_2O$
(25) $HNO_3 \rightleftharpoons NO_2 + H_2O + O^\circ$
(26) $HCl + HNO_3 \rightleftharpoons Cl^\circ + NOCl + H_2O$
(27) $Bi(OH)_3 + Na_2SnO_2 \rightleftharpoons NaSnO_3 + H_2O + Bi^\circ$
(28) $Na_2O_2 + H_2O \rightleftharpoons NaOH + O^\circ$
(29) $Bi_2S_3 + HNO_3$ (dil.) $\rightleftharpoons Bi(NO_3)_3 + NO + H_2O + S^\circ$
(30) $FeCl_2 + H_2O_2 + HCl \rightleftharpoons FeCl_3 + H_2O$

6. Write the balanced molecular equations for the following oxidation-reduction reactions:

(31) $Fe_2(SO_4)_3 + Zn^\circ \rightleftharpoons FeSO_4 + ZnSO_4$
(32) $FeCl_3 + KI \rightleftharpoons FeCl_2 + KCl + I^\circ$
(33) $HgCl_2 + SnCl_2 \rightleftharpoons Hg_2Cl_2 + SnCl_4$
(34) $FeSO_4 + KMnO_4 + H_2SO_4 \rightleftharpoons Fe_2(SO_4)_3 + K_2SO_4 + MnSO_4 + H_2O$
(35) $Na_2C_2O_4 + KMnO_4 + H_2SO_4 \rightleftharpoons Na_2SO_4 + K_2SO_4 + MnSO_4 + H_2O + CO_2$
(36) $K_2Cr_2O_7 + KI + H_2SO_4 \rightleftharpoons K_2SO_4 + Cr_2(SO_4)_3 + H_2O + I^\circ$
(37) $MnO_2 + H_2C_2O_4 + H_2SO_4 \rightleftharpoons MnSO_4 + H_2O + CO_2$
(38) $SnCl_2 + I_2 + HCl \rightleftharpoons SnCl_4 + HI$
(39) $Ti_2(SO_4)_3 + Fe_2(SO_4)_3 \rightleftharpoons Ti(SO_4)_2 + FeSO_4$
(40) $V_2O_5 + KI + HCl \rightleftharpoons V_2O_4 + KCl + H_2O + I^\circ$
(41) $Mn(NO_3)_2 + (NH_4)_2S_2O_8 + H_2O \rightleftharpoons HMnO_4 + HNO_3 + H_2SO_4 + (NH_4)_2SO_4$
(42) $Mn(NO_3)_2 + KIO_4 + H_2O \rightleftharpoons HMnO_4 + HNO_3 + KIO_3$
(43) $FeCl_2 + Ce(SO_4)_2 + HCl \rightleftharpoons FeCl_3 + Ce_2(SO_4)_3 + H_2SO_4$
(44) $MnO_2 + FeSO_4 + H_2SO_4 \rightleftharpoons MnSO_4 + Fe_2(SO_4)_3 + H_2O$
(45) $KMnO_4 + H_2S + HCl \rightleftharpoons MnCl_2 + KCl + H_2O + S^\circ$

7. Make a table of twelve common oxidizing agents which includes the following: (*a*) element or radical involved, (*b*) valence of element, (*c*) reduced form, (*d*) new valence, (*e*) decrease in valence, and (*f*) gain in electrons.

8. Make a table of twelve common reducing agents similar to the one prepared for oxidizing agents.

CHAPTER VI

GASES

THE LAWS OF GASES

We have already learned that matter may exist in three states: solid, liquid, or gaseous. A gas may be defined as matter which fills completely and to a uniform density any available space. Gases have no definite shape or volume, they are light in weight, their viscosity is small, and they mix in all proportions.

The volume of solids and liquids may be easily and accurately measured. This is because their volume is altered only very slightly by changes in temperature and pressure. Except in the most refined measurements, ordinary changes of temperature and pressure are neglected in the measurement of volumes of solids and liquids. But the temperature and pressure coefficients of gases are very large and must always be taken into account. In measuring a given quantity of gas it is necessary to measure the volume, temperature, and pressure accurately. Then, if the density be known, the weight may be accurately obtained. Examples will be given after a consideration of the gas laws. It should be obvious from the above statement that gaseous volumes may be compared only when they are all at the same temperature and pressure. Also, gas densities vary with the temperature and pressure. It is therefore necessary to adopt a **standard temperature** and a **standard pressure.** The standard temperature is 0° C. and the standard pressure is 760 mm. of mercury. These conditions are frequently referred to as **normal temperature and pressure** and abbreviated N.T.P., or if the word **standard** is used, the abbreviation becomes S.T.P.

The laws which express the behavior of gases are relatively simple.

Boyle's Law. In 1660 Robert Boyle discovered that, when air was compressed or expanded at constant temperature, "The pressures and expansions were in reciprocal proportion." This observation was later found to apply to all gases and is now known as **Boyle's law.** It is stated as follows: **When the temperature is constant, the pressure of a gas varies inversely as its volume.** Or the law may be stated: **At constant temperature, the volume of a given mass of a gas is inversely proportional to the pressure to which it is subjected.** The law may be expressed mathematically as follows:

$$V \propto \frac{1}{P}$$

To change the variation into an equation, a proportionality constant, K, must be introduced:

$$V = K\frac{1}{P}$$

or

$$PV = K$$

The function of such a constant is to relate the magnitudes of the two variables, pressure and volume, to each other and also the units in which they are expressed. Suppose that we have 100 liters of a certain gas at 750 mm. Applying Boyle's law:

$$100 \propto \frac{1}{750}$$

$$100 = K\frac{1}{750}$$

$$K = 75{,}000$$

If we know the value of the constant, K, then the volume of this gas sample may be calculated at any pressure, and *vice versa.*

Boyle's law is sometimes expressed in another way. If V_1 is the volume of a given sample of gas at pressure P_1, and V_2 is its volume at pressure P_2, then

$$\frac{V_1}{V_2} = \frac{P_2}{P_1}$$

$$P_1V_1 = P_2V_2$$

An inspection of the equation shows that, if the pressure on the gas be doubled, the volume is halved, etc. Volume changes due to changes in pressure may be readily calculated by this law.

Example. One hundred cubic centimeters of oxygen are collected under a pressure of 750 mm. of mercury. What would the volume be under 770 mm.?

By inspection we note that the pressure is raised, therefore the volume will become smaller; hence we must multiply the volume by a fraction less than unity:

$$V = 100 \times \frac{750}{770} = 97.4 \text{ cc.}$$

Temperature Scales. As stated above, temperature changes produce large changes in gas volumes, but before discussing the law governing these changes let us consider the several common temperature scales:

1. The Fahrenheit Scale, ° F.
2. The Centigrade Scale, ° C.
3. The Absolute Scale, ° A.

The two common reference points on temperature scales are the melting of ice (32° F. or 0° C.) and the boiling of water (212° F. or 100° C.) under standard atmospheric ressure. On the Fahrenheit scale there is a difference of 180° between the melting of ice and the boiling of water, and on the Centigrade scale there is 100° difference between these points. Hence, $1° \text{ F.} = \frac{100}{180} = \frac{5}{9}$ of 1° C.

The formulas for converting one temperature to the other are:

$$° \text{F.} = 9/5(° \text{C.}) + 32, \quad \text{and} \quad ° \text{C.} = 5/9(° \text{F.} - 32)$$

It is interesting to note that −40° is the same on both scales. Prove this to yourself by inserting −40° in the above formulas.

Experiment has shown that a given mass of gas, at constant pressure, will increase or decrease 1/273.1 of its volume at 0° C. for every degree through which it is heated or cooled. The zero point therefore would be −273.1° C. This is called the **absolute zero** of temperature. To convert degrees Centigrade to degrees Absolute, add 273.1 to the degrees Centigrade: ° A. = ° C. + 273.1. In making volume corrections for changes in temperature, ° F. and ° C. must always be converted to ° A.

Theoretically, a gas would have no volume at the absolute zero, but as a matter of fact all known gases become liquid or solid before this temperature is reached. Helium, the most difficult gas to liquefy, boils at 4.5° A., or −268.6° C. By rapid evaporation of liquid helium, Kammerlingh Onnes, a Dutch physicist, has succeeded in reaching a temperature of 0.82° A. In 1935 scientists at Leyden reached a temperature within 0.005° of absolute zero.

The Law of Charles. This law was discovered by Charles in 1787 and later discovered independently by Dalton (1801) and by Gay-Lussac (1802). It may be stated thus: **At constant pressure, the volume of a given mass of a gas is directly proportional to the absolute temperature.** Expressed mathematically,

$$V \propto T,$$

$$V = KT,$$

$$\frac{V}{T} = K,$$

where V is the volume, T is the absolute temperature, and K is a proportionality constant.

If the volumes of a given mass of a gas at two different temperatures are to be compared, we have

$$\frac{V_1}{V_2} = \frac{T_1}{T_2}$$

A corollary to the laws of Boyle and of Charles may be stated as follows: **At constant volume, the pressure of a given mass of a gas varies directly with its absolute temperature.** Stated mathematically,

$$P \propto T$$

$$P = KT$$

If we are to compare the pressures of a given mass of a gas at two different temperatures, the equation becomes:

$$\frac{P_1}{P_2} = \frac{T_1}{T_2}$$

Examples. 1. Twenty-five liters of nitrogen are collected at 22° C. What volume would the gas occupy at 0° C.?

Converting the temperatures to the absolute scale, we have 295° A. and

273° A. Since the gas is cooled, its new volume will be less than 25 liters; hence, 25 must be multiplied by a fraction less than unity.

$$V = 25 \times \frac{273}{295} = 23.1 \text{ liters}$$

2. One hundred liters of hydrogen are measured at 750 mm. pressure and at 15° C. What would be the pressure if the temperature should be raised to 25° C., the volume remaining unchanged?

An increase in temperature would cause an increase in pressure, hence 750 must be multiplied by a fraction greater than unity.

$$P = 750 \times \left(\frac{25 + 273}{15 + 273}\right) = 776 \text{ mm.}$$

The General Gas Equation. There are three variables which determine the state of any gas, namely, **volume, pressure,** and **temperature.** In discussing the above gas laws, we considered how one of these varied with another if the third was kept constant. In practice, all three factors frequently vary. It is therefore desirable to derive an expression to handle such changes. Suppose that we have a volume V_1 of a gas at pressure P_1 and temperature (absolute) T_1. Now suppose we change the conditions so that the volume becomes V_2, the pressure P_2, and the temperature T_2. What will be the relationship between the first set of conditions and the second set? It will simplify our problem if we carry out the change in two steps. It makes no difference which step is taken first, but suppose the temperature is kept constant at T_1 and the pressure is raised to P_2. Let the new volume be designated V^1. Then,

$$\frac{V_1}{V^1} = \frac{P_2}{P_1} \tag{1}$$

Now suppose we raise the temperature to T_2, holding the pressure at P_2. Then,

$$\frac{V^1}{V_2} = \frac{T_1}{T_2} \tag{2}$$

By combining equations (1) and (2) we obtain an expression known as the **general gas equation:**

$$\frac{V^1}{V_2} = \frac{T^1}{T_2} \times \frac{P_2}{P_1} \tag{3}$$

If we know any five of these variables, the sixth can readily be calculated by substituting in the above equation (3). An example will illustrate. Ten liters of hydrogen are measured at 20° C. and 740 mm. pressure. If the temperature is lowered to 0° C. and the pressure raised to 760 mm., what will be the volume occupied by the gas?

$V_1 = 10$ liters $\quad P_1 = 740$ mm. $\quad T_1 = 293°$ A.
$V_2 = ?$ $\quad P_2 = 760$ mm. $\quad T_2 = 273°$ A.

Substituting in the general gas equation (3):

$$\frac{10}{V_2} = \frac{293}{273} \times \frac{760}{740}$$

$$V_2 = 10 \times \frac{273}{293} \times \frac{740}{760} = 9.1 \text{ liters}$$

The Fundamental Gas Equation. By combining the expressions for the laws of Boyle and of Charles, we have

$$V \propto \frac{T}{P}$$

and introducing a proportionality constant, K,

$$V = K\frac{T}{P}$$

or

$$PV = KT$$

If this equation is applied to one mol of gas (i.e., the molecular weight of the gas taken in grams), R, the **molar gas constant**, may be used in place of the constant K. By introducing the factor n, which represents the number of gram-molecules of gas taken, we obtain the general expression

$$PV = nRT$$

and when

$$n = 1$$

$$PV = RT$$

This is the **fundamental gas equation.** R, the molar gas constant, may be expressed in several different energy units: (1) liter-atmospheres per degree, (2) cubic centimeter-atmospheres per degree, (3) joules per degree, (4) calories per degree. It is suggested that the student calculate the numerical values of R in these four units. (Consult a textbook on physical chemistry.)

Since n, the number of gram-molecules, is obtained by dividing the **weight** of gas taken by its **molecular weight**, the gas equation may be written

$$PV = \frac{wRT}{M}$$

where w is the weight of gas in grams and M is its molecular weight.

Deviations from the Gas Laws and van der Waals' Equation. Many carefully performed experiments by a number of investigators show that gases do not strictly obey the fundamental gas equation, $PV = nRT$, the deviations depending on the nature of the gas and the conditions of temperature and pressure. The gas laws are more nearly obeyed the higher the temperature, the lower the pressure, and the further the gas is removed from its critical state. (See page 55.) An **ideal** or **perfect gas** is one that obeys the fundamental gas equation, but all real gases deviate from the **ideal** and for the same reason. Since in the above equation the product PV is constant at a given temperature, by plotting pressures as abscissas and the corresponding PV values as ordinates, a perfect gas would give a straight line parallel to the axis of abscissas.

Natterer pointed out that PV for hydrogen at room temperature is too high, and Budde suggested that the deviation was due to the volume occupied by the molecules themselves. Denoting the total volume occupied by the molecules by b, the corrected gas equation becomes:

$$P(V - b) = RT$$

where b is a constant for each gas. This equation, though satisfactory for hydrogen, fails when applied to many other gases. All gases, under the proper conditions, show a minimum in their PV vs. P curves. That is to say, at certain temperatures the gases are more compressible than a perfect gas under low pressures, and less compressible under high pressures. Hence, PV passes through the value required by Boyle's law. In 1879, van der Waals showed that at high pressures the volume of a gas is less than the calculated value and said that this effect was due to mutual attraction of the molecules. That is to say, the gas behaves as if it were subjected to a pressure greater than that actually applied. It was shown that this attraction is inversely proportional to the square of the volume of the gas. If a is taken as the attraction when the volume is one liter, than a/V^2 is the attraction for any other volume. Since the attraction acts with the external pressure, the total or corrected pressure is $P + a/V^2$. Correcting the gas equation for both volume and pressure, we have

$$(P + a/V^2)(V - b) = RT$$

This is called van der Waals' equation, and it is applicable not only to highly compressed gases, but also to liquids. It should be pointed out that, when V is large, both a/V^2 and b become negligible, and van der Waals' equation reduces to the simple gas equation, $PV = RT$. From this it follows that any influence tending to increase V will cause a gas to approach more nearly the ideal condition. Hence, an increase in temperature at constant pressure, or a diminution in pressure at constant temperature, causes a gas more nearly to obey the simple gas laws. At the pressures and temperatures generally used in the laboratory, the deviations of gases from the gas laws are not greater than the ordinary errors of observation.

Mixtures of Gases: Dalton's Law. Gases possess the property of mixing freely in all proportions. In a mixture of gases, each gas distributes itself throughout the containing vessel just as if no other gas were present. The properties of a mixture of gases are the sums of the corresponding properties of its components. In 1807, Dalton enunciated an important law. It is known as Dalton's **law of partial pressures** and may be stated thus: **In a mixture of gases, provided they do not combine chemically, the pressure is equal to the sum of the pressures that would be exerted by each gas if it were allowed to fill the containing vessel alone.** In other words, the pressure of each gas is independent of the pressures exerted by the other gases. The pressure which each gas exerts is called its **partial pressure** and is proportional to its concentration. In brief, the **total pressure** of a gaseous mixture is equal to the sum of the **partial pressures.**

Dry air is a mixture of one-fifth of oxygen and four-fifths of nitrogen (including about one per cent of certain rare gases) by volume. A better statement would be to say that a liter of dry air under one atmosphere of pressure (760 mm. of mercury) contains a liter of oxygen under a partial pressure of one-fifth of an atmosphere and a liter of nitrogen under a partial pressure of four-fifths of an atmosphere.

A gas collected over a liquid always contains some of the vapor of the liquid. When the gas is collected over mercury, the amount of mercury vapor is so minute that it is disregarded, but when, for example, a gas is collected over water, the water vapor is appreciable. The partial pressure of the water vapor is called **aqueous tension,** or the **vapor pressure of water.** The volume of a gas measured over water is larger than it would be if the gas were dry; hence, to reduce to the dry condition, the aqueous tension is subtracted from the corrected barometric pressure. The aqueous tension, of course, increases with the temperature. A table of aqueous tensions over a wide range in temperature has been prepared and may be found in any handbook on chemistry or physics.

Example. One hundred cubic centimeters of hydrogen are collected over water at 25° C. and 750 mm. What volume would the hydrogen occupy when dry and at S.T.P.? The aqueous tension at 25° C. is 23.7 mm.

$$V_{\text{S.T.P.}} = 100 \times \frac{273}{298} \times \frac{(750 - 23.7)}{760} = 87.5 \text{ cc.}$$

Diffusion of Gases: Graham's Law. Under ordinary conditions gases diffuse into one another until the gaseous mixture is uniform in composition. The law governing the rates of diffusion of gases was discovered by Graham in 1833; it states that **the rate or speed of diffusion of a gas is inversely proportional to the square root of its density,** or, otherwise expressed, $r = 1/\sqrt{d}$, where r is the rate of diffusion and d is the density of the gas. For example, the density of hydrogen is approximately $\frac{1}{16}$ as great as that of oxygen. Hence, hydrogen diffuses four times as fast as does oxygen. The densities are in the proportion 1 : 16. The inverse ratio of the square roots of the densities is $\sqrt{16} : \sqrt{1}$, or 4 : 1, which is the ratio for the rates of diffusion of hydrogen and oxygen.

Graham's law may be used to determine the molecular weight of a gas or vapor. If the rates of diffusion of two gases be designated by r and r', and their densities by d and d', respectively, then their relative speeds may be expressed as follows: $r : r'$

$= \sqrt{1/d} : \sqrt{1/d'}$ or, $r : r' = \sqrt{d'} : \sqrt{d}$. Since the molecular weight of a gas is proportional to its density, the equation may be written $r : r' = \sqrt{M'} : \sqrt{M}$, where M and M' are the molecular weights of the two gases. In practice, the time required for a known volume of a gas to pass through a small opening is measured instead of the actual diffusion rate. The time, t, is **inversely** proportional to the rate and **directly** proportional to the square root of the molecular weight of the gas. Hence, for any two gases the equation may be written: $t : t' = \sqrt{M} : \sqrt{M'}$. If some gas of known molecular weight, M, for example oxygen, be taken as standard and its time, t, of outflow and that of an equal volume of another gas, t', be measured, then the molecular weight, M', of the second gas may be calculated by substitution in the equation:

$$t : t' = \sqrt{32} : \sqrt{M'}$$

where $M = 32$, the molecular weight of oxygen. This equation may be written

$$M' = \frac{t'^2 \cdot 32}{t^2}$$

Obviously in experiments of this kind the diffusions must be compared at the same temperature.

Density of Gases. The **absolute density** D of a gas is determined by measuring the mass M of a certain volume V at a known temperature T, and then dividing the mass by the volume:

$$D = \frac{M}{V}$$

In scientific work the absolute density of a gas is usually expressed in grams per milliliter (or cubic centimeter) or in grams per liter at standard conditions of temperature and pressure: i.e., 0° C. and 760 mm. of mercury. The **relative density** or **specific gravity** of a gas is the ratio of the weight of a given volume to the weight of an equal volume of another gas taken as standard and considered as unity. Both gases must be measured at the same temperature and pressure. Oxygen, hydrogen, and air are the gases generally taken as standards.

Example. One liter of ammonia, NH_3, weighs 0.771 g. at S.T.P. What is the specific gravity (relative density) of ammonia referred (*a*) to air, (*b*) to oxygen, and (*c*) to hydrogen? At S.T.P., one liter of these gases weighs 1.293 g., 1.429 g., and 0.08987 g., respectively.

Referred to air: $$\text{Sp. gr. } NH_3 = \frac{0.771}{1.293} = 0.597.$$

Referred to oxygen: $$\text{Sp. gr. } NH_3 = \frac{0.771}{1.429} = 0.540.$$

Referred to hydrogen: $$\text{Sp. gr. } NH_3 = \frac{0.771}{0.08987} = 8.58.$$

Gas Density and Molecular Weight. In determining the atomic weights of the elements, oxygen is taken as the standard and given an arbitrary value of 16 as its atomic weight (see page 9). Likewise, in determining molecular weights, oxygen is taken as standard and is given a molecular weight of 32 as it is a diatomic gas. Now it has been shown by experiment that 32 g. of oxygen occupies a volume of 22.412 liters at 0° and 760 mm. pressure after correcting for deviations from the perfect gas laws. Hence, to determine the molecular weight of any gas it is necessary only to find the weight of 22.412 liters of the gas at 0° and 760 mm. pressure. This is an application of Avogadro's law which states that equal volumes of all gases, under the same conditions of temperature and pressure, contain the same number of molecules. In practice, any convenient volume of gas or vapor is weighed at any temperature and under any pressure. The weight of 22.412 liters under standard conditions is then calculated. An alternative method is to determine the volume of a known weight of the gas or vapor under definite conditions of temperature and pressure, and then calculate the weight of 22.412 liters at S.T.P.

Some vapors undergo dissociation upon being heated. The extent or degree of dissociation at any one temperature can be determined easily by measuring the vapor density, which in a dissociating vapor decreases with increase in temperature.

THE KINETIC THEORY OF GASES

We have already learned that matter may exist in any one of three states: solid, liquid, gaseous. We have also learned that masses of matter are composed of extremely minute particles called molecules, each one of which has properties identical with those of the whole mass. Furthermore, we have learned that the molecules consist of atoms of elements combined in definite numbers. There is a vast amount of experimental evidence that the molecules of matter are in continuous motion. The energy of motion of molecules is called **kinetic energy.** The word kinetic is derived from the Greek word *κινητικός*, which means "of motion" or "pertaining to motion," hence the **kinetic-molecular theory.**

It is believed that all matter has a discontinuous structure; that is, it is made up of separate or distinct particles. All matter is compressible. Solids may be converted into liquids and liquids may be evaporated into gases or vapors. Solids will absorb both liquids and gases. The kinetic-molecular theory is applied to matter in all three of its states, but in a study of the theory it is best to begin with gases, since they are characterized by very simple and uniform behavior with respect to temperature and pressure. As a result of certain observed facts and the application of the kinetic theory, the following deductions may be made:

1. A gas is composed of submicroscopic particles, called molecules, which are all alike.
2. Gas molecules are moving rapidly and continuously in a random fashion, and are relatively far apart except at very high pressures.
3. The speed at which gas molecules move is inversely proportional to the square root of their mass.
4. The pressure exerted by a gas is due to the incessant bombardment of the walls of the containing vessel by the molecules and is proportional to the concentration of the gas.
5. The collisions of gas molecules may be regarded as perfectly elastic; i.e., they lose none of their kinetic energy upon impact with other molecules or with the walls of the container, at the same temperature.
6. The average kinetic energy of gas molecules is directly proportional to the absolute temperature. In other words, a rise in temperature increases the speed of the molecules and hence increases their kinetic energy. When a gas expands against an external force it does work at the expense of the kinetic energy of its molecules, and hence it loses heat.

All the above deductions are confirmed by experiment. Gases are homogeneous as shown by analysis. They are highly compressible, diffuse rapidly, exert a pressure on the walls of the containing vessel, do not settle, and obey (except at high pressures and at low temperatures)•Boyle's law, Charles' law, and Graham's law.

Starting with the above assumptions, it is possible to derive an equation from which the gas laws may be deduced. From lack of space, we simply state the fundamental equation of the kinetic theory of gases. It is $PV = \frac{1}{3}nmu^2$, where n is the number of molecules, each having a mass m, and u is their mean velocity. From this equation the laws of Boyle, Charles or Gay-Lussac, Avogadro, and Graham can be deduced. It is suggested that the student consult a textbook on physical chemistry and deduce these laws after he has derived the kinetic equation.

Specific Heat of Gases. As we have just seen, the kinetic theory assumes that gas molecules are simple units and that they can absorb only energy which is used in changing their velocities. In actuality this assumption is seldom true, and a study of the specific heats of gases gives us a greater insight into their behavior. The heat capacity of a substance is the ratio of the amount of heat supplied to the temperature rise. The specific heat is the heat capacity per gram of the substance. More heat will be required to raise a given mass of gas one degree when the gas is heated at constant pressure than when it is heated at constant volume. The reason for this is that, when heated at constant pressure, the gas expands and hence does work against the atmosphere. The cause of this difference between the two specific heats of a gas was discovered by Mayer in 1841 and led him to calculate the mechanical equivalent of heat and to formulate clearly the first law of thermodynamics (1842), or the principle of the conservation of energy; i.e., energy cannot be created or destroyed.

The difference between the specific heat at constant pressure, C_p, and the specific heat at constant volume, C_v, may be calculated from the gas law

$$PV_1 = RT_1,$$

where V_1 is the volume of 1 mol of gas at temperature T_1, and R is the molar gas constant. Upon heating the gas at constant pressure to temperature T_2, the volume expands to V_2 and the work thus performed is equal to the product of the pressure and the increase in volume, or

$$P(V_2 - V_1) = R(T_2 - T_1)$$

If $T_2 - T_1 = 1°$, the equation becomes

$$P(V_2 - V_1) = R$$

The molar heat capacity of a gas is equal to its specific heat multiplied by its molecular weight. The difference between the molar heat at constant pressure, C_p, and the molar heat at constant volume, C_v, is equivalent to the external work performed when the temperature of 1 mol of gas is raised 1°. Hence,

$$C_p - C_v = Mc_p - Mc_v = P(v_2 - v_1) = R = 1.987 \text{ cal.}$$

That is to say, the difference between the two molar heat capacities, C_p and C_v, of any gas is equal to the gas constant R, i.e., approximately 2 cal. per degree.

By means of the fundamental kinetic equation, the molar heat capacity, C_v, for monatomic gases is calculated to be 3 cal. per degree. Hence, $C_p = C_v + 2 = 5$ cal. per degree. The ratio

$$V = \frac{C_p}{C_v} = \frac{5}{3} = 1.66$$

is in excellent agreement with experimental facts. For polyatomic gases the ratio becomes less than 1.66 and approaches the limiting value 1 as the complexity of the molecule increases. This is because in the polyatomic gases the heat energy supplied is used not only in increasing the translational kinetic energy of the molecules (as in monatomic gases) but also in increasing the energy of rotation and of vibration of the atoms within the molecule.

Avogadro's Hypothesis. In 1811, Avogadro, professor of physics at the University of Turin, in an attempt to explain the uniform behavior of gases, made the assumption that **equal volumes of all gases under the same conditions of temperature and pressure contain the same number of molecules.** The hypothesis was based mainly on **Gay-Lusac's law of combining volumes,** which was enunciated in 1808: **When gases enter or leave chemical combination, the volumes absorbed, or liberated, are in simple ratios to one another.** All volumes must, of course, be measured at the same temperature and pressure. When carbon monoxide is burned (oxidized) to carbon dioxide the reaction is expressed as follows:

$$\begin{array}{ccccc} 2CO & + & O_2 & \rightarrow & 2CO_2 \\ \text{Carbon} & & \text{Oxygen} & & \text{Carbon} \\ \text{monoxide} & & \text{1 volume} & & \text{dioxide} \\ \text{2 volumes} & & & & \text{2 volumes} \end{array}$$

It is seen that, when the above reaction takes place, the volumes of the gases are related to one another in the proportion 2 : 1 : 2. Similarly, when hydrogen and oxygen unite to form water (steam), the volume ratio is 2 : 1 : 2, and the reaction is expressed thus:

$$2H_2 + O_2 \rightarrow 2H_2O_{(\text{steam})}$$

Critical Temperature and Critical Pressure. If a gas is cooled and the pressure on it is increased, a temperature may finally be reached at which the gas suddenly changes to a liquid. This temperature, above which it is impossible to liquefy the gas, is called its **critical temperature** (C.T.), and the pressure required to liquefy the gas at its C.T. is called the **critical pressure** (C.P.).

Some Interesting Gas Data. By application of the gas laws and the kinetic theory it has been possible to compute some interesting data concerning molecules.

1. *Size of Molecules.* As might be expected, the molecules of different gases vary considerably in size, yet not as much as might be expected when it is remembered that they must be regarded as complex systems and not at all like smooth balls. As a matter of fact, the size of molecules is probably not a very definite thing, for we do not know how far the sphere of influence extends. However, some calculations have been made, and a few are given here:

Molecule	Volume in Cubic Centimeters
Hydrogen	4.8×10^{-23}
Carbon dioxide	6×10^{-23}
Water	3×10^{-23}

2. *Number of Molecules.* The number of molecules of gas per liter at S.T.P. has been determined by several reliable methods and found to be 2.7×10^{22}, with a probable error of less than one per cent.

3. *Average Spacing of Molecules.* Since the number of molecules in 1 cc. of a gas is 2.7×10^{19}, by taking the cube root of this we obtain the number in one linear centimeter, i.e., 3×10^{6}. The

average distance apart, from center to center, is therefore 3.3 × 10^{-7} cm. The **actual** distance apart of any two molecules varies widely and is constantly changing.

4. *Mean Free Path in Gases.* In a study of the theory of gases one of the most important points to be considered is the average distance molecules travel between collisions. This distance is called the **mean free path.** It must not be confused with the **average spacing** of molecules. A molecule may travel several times the average spacing distance before colliding with another molecule. The mean free path for any gas under S.T.P. was first calculated by James Clerk Maxwell (1860) and is not far from 1×10^{-5} cm. Several different methods give values in close agreement with Maxwell's calculation. Since the average spacing of molecules is 3.3×10^{-7} cm., it follows that a molecule will pass about thirty of its neighbors before finally colliding with one. In other words, the mean free path of molecules is about thirty times their average spacing. Yet a hydrogen molecule collides, at room temperature, with other hydrogen molecules about 10,000,000,000 times per second!

5. *Velocity of Molecules.* Hydrogen is the lightest molecule and has the greatest velocity. The average velocities are given for several gases at 0° C.:

Gas	Velocity (meters per second)
Hydrogen	1,859
Nitrogen	492
Oxygen	465
Carbon dioxide	396
Chlorine	310

PROBLEMS

1. If the pressure on 10 liters of hydrogen is lowered from 755 mm. to 740 mm., what will be the new volume of the gas?

Ans. 10.2 l.

2. Five hundred cubic centimeters of nitrogen are collected under a pressure of 752 mm. of mercury. What would the volume be under 775 mm.?

Ans. 485 cc.

3. (*a*) What volume (S.T.P.) of hydrogen sulfide can be obtained by the action of hydrochloric acid on 2.5 g. of ferrous sulfide? (*b*) What would be the volume at 748 mm. of pressure?

Ans. (*a*) 0.64 l.
(*b*) 0.65 l.

4. Two hundred liters of oxygen are measured at S.T.P. If the temperature be raised to 25° C., what would be the new volume?

Ans. 218 l.

5. How many liters of carbon dioxide can be obtained, at 20° C. and 771 mm., by the action of a strong acid on 25 g. of marble?

Ans. 5.9 l.

6. One hundred cubic centimeters of chlorine are measured at 75° F. and 1.2 atmosphere of pressure. Calculate the volume at standard conditions.

Ans. 110 cc.

7. What volume of oxygen, measured at 70° F. and 1.1 atmosphere, is available in 10 liters of pure, dry air measured at 80° F. and 0.9 atmosphere?

Ans. 1.69 l.

8. Ten liters of ammonia are measured at 30° C. and 765 mm. of pressure. What would be the pressure if the temperature be lowered to 20° C., the volume remaining unchanged?

Ans. 740 mm.

9. A certain quantity of a gas is measured at 25° C. and 748 mm. of pressure. Upon being heated at constant volume, the pressure was found to increase to 810 mm. What was the temperature rise?

Ans. 25°.

10. Fifty liters of nitrogen are collected over water at 20° C. and 780 mm. of pressure. Calculate the volume of dry gas at S.T.P.

Ans. 47 l.

11. What volume of carbon dioxide can be obtained by igniting at a high temperature 5 g. of marble, the gas being collected over mercury at 100° F. and 1.1 atmosphere?

Ans. 1.16 l.

12. Five grams of marble are heated at a high temperature and the carbon dioxide collected over water. The temperature is 100° F. and the pressure 1.1 atmosphere. Calculate the volume occupied by the gas. Compare this volume with that in problem 11.

Ans. 1.23 l.

13. Calculate the pressure at which 5.0 g. of chlorine occupy 30 liters at 25° C. Use the equation $PV = wRT/M$. R in liter-atmospheres per degree is 0.082.

Ans. 0.057 atmos.

14. What weight of carbon tetrachloride is required to yield sufficient vapor to fill a space of 10 liters at 100° C. and 740 mm.? Solve by two methods.

Ans. 49 g.

15. A liter of ammonia weighs 0.7708 g. at S.T.P. What is its density at 20° C. and 770 mm.?

Ans. 0.728 g. per l.

16. What volume of hydrogen sulfide at 25° C. and 753 mm. will be required to precipitate as sulfides 50 mg. of lead and 100 mg. of tin (ous) from a solution of salts of these metals? (Assume no loss of H_2S.)

Ans. 27 cc.

17. How many liters of ammonia gas at 22° C. and 768 mm. can be obtained from 10 g. of ammonium sulfate?

Ans. 3.6 l.

18. If 100 cc. of hydrogen diffuses through a small opening in 5.32 minutes, what would be the time required for an equal volume of ammonia to pass through under the same conditions?

Ans. 15.5 min.

19. Compare the diffusion rates of the following gases with that of air: (*a*) helium, (*b*) nitrogen, (*c*) chlorine, (*d*) hydrogen chloride, and (*e*) sulfur dioxide.

20. Calculate the specific gravity of each of the following gases referred to air: (*a*) carbon monoxide, (*b*) carbon dioxide, (*c*) hydrogen sulfide, (*d*) ammonia, and (*e*) chlorine. At S.T.P., one liter of these gases weighs: air, 1.293 g.; CO, 1.2500 g.; CO_2, 1.9766 g.; H_2S, 1.539 g.; NH_3, 0.7708 g.; Cl_2, 3.2200 g.

Ans. (*a*) 0.965. (*d*) 0.595.
(*b*) 1.53. (*e*) 2.49.
(*c*) 1.19.

CHAPTER VII

LIQUIDS

The Kinetic Theory of Liquids. Matter in the liquid state occupies an intermediate position between gases on the one hand and solids on the other. A given mass of gas is capable of indefinite expansion and will therefore **fill completely** all available free space; a liquid, on the other hand, can occupy only a definite volume (at a given temperature). It does, however, take the shape of the containing vessel, a property which is not shared by solids. Liquids then are fairly loose aggregates of molecules which probably glide over each other in curved courses. Fundamentally there is no difference between the liquid and the gaseous state and they become identical at the **critical temperature,** i.e., the temperature above which the gas cannot be liquefied no matter how much pressure is exerted upon it. The pressure required to liquefy a gas at its critical temperature is called the **critical pressure,** and the volume occupied by a mol of the gas or liquid at the critical temperature and pressure is the **critical volume.**

Cohesion is greater in liquids than in gases, and they have greater densities than gases since their molecules are closer together. From this it follows that liquids diffuse more slowly than gases. But liquids do diffuse, as can be strikingly demonstrated by embedding one end of a crystal of potassium permanganate in a little paraffin wax on the under side of a watch-glass and then allowing the exposed end of the crystal to dip into water contained in a tall glass cylinder. The crystal slowly dissolves and forms a bright purple solution which gradually diffuses down through the water thereby coloring it. Diffusion proceeds fairly slowly until finally a homogeneous solution is obtained as indicated by the uniform pink color. This will probably require several days or longer. If samples of the solution were carefully withdrawn from the cylinder at different heights and the amount of potassium permanganate per unit volume of solution determined by evaporating off the water and weighing the residue, it would be found that the permanganate had uniformly distributed itself throughout the liquid. The fact that the water can be driven off by evaporation also proves that the molecules in a liquid are in motion. This motion is due to kinetic energy of the molecules. Some liquids evaporate faster than others. Liquids with low boiling-points evaporate (at a given temperature) faster than those with high boiling-points. In a given liquid, not all molecules possess the same amount of kinetic energy, but the molecules as a whole have a mean value. Some of the molecules that come to the surface of the liquid will have so much kinetic energy that they leave the liquid never to return; that is, they pass beyond the sphere of molecular attraction. Since the warmest molecules possess the greatest amount of kinetic energy, the temperature of a liquid becomes less as evaporation proceeds. Those molecules leaving the surface of the liquid with less kinetic energy, or in other words with less speed, than that required to carry them beyond the range of molecular attraction would be pulled back into the liquid. Therefore, when a liquid evaporates, two opposite processes are in operation—evaporation and condensation. In an open vessel, the evaporation process is the more rapid and becomes still more rapid in a draft or when suction is applied. In a closed vessel at a constant temperature the rate of evaporation, or the number of molecules leaving the liquid per unit time, will be constant, and the rate of condensation, or the number of molecules returning to the liquid per unit time, will steadily increase until the two processes exactly balance one another. Such a condition of balanced activities is known as a **kinetic equilibrium.** Note that such an equilibrium is not **static,** for both operations (evaporation and condensation) are still going on, the one just balancing the other. The vapor which is in equilibrium with the liquid phase is said to be **saturated,** and the pressure exerted by it is known as the **vapor pressure.** This equilibrium is dependent upon the temperature. The temperature at which liquid and vapor are in equilibrium under 760 mm. of pressure is called the **boiling-point** of the liquid. The **absolute boiling temperature** of a liquid is approximately two-thirds of its critical temperature. This interesting empirical relation was pointed out by Guldberg and Guye (1890).

To sum up, there are three things characteristic of a **state of equilibrium:**

1. There are **always two opposing processes** which, when equilibrium is reached, exactly balance each other. In the above illustration one of these processes is the hail of molecules leaving the liquid, which is constant throughout. It represents the **vapor tension of the liquid.** The other process is the hail of returning molecules, which increases in rate steadily as the concentration of vapor increases. It is called the **vapor pressure of the vapor,** and when it equals the vapor tension of the liquid, **equilibrium** is established. With water, the equilibrium may be represented by the following equation:

$$H_2O_{(liquid)} \rightleftharpoons H_2O_{(vapor)}$$

2. **At equilibrium, both processes are still in full operation.** Equilibrium is a state of balanced activities and not a state of rest.

3. **For every small change in the conditions, there is always instantly a corresponding change in the state of the system.**

Isothermals. If gases be subjected to various pressures at constant temperature and the resulting volumes be plotted as abscissas and the corresponding pressures as ordinates, the curves thus obtained are called **isothermals.** For gases such as nitrogen, the inert gases, etc., which obey Boyle's law, the isothermals at different temperatures will be a series of right-angled hyperbolas. But for easily liquefied gases, for example, carbon dioxide (see Fig. 1[1]), the isothermals are hyperbolic or nearly hyperbolic at higher temperatures and then deviate more and more as the temperature becomes lower. At the critical temperature 30.92°, the isothermal curve is almost horizontal for a short

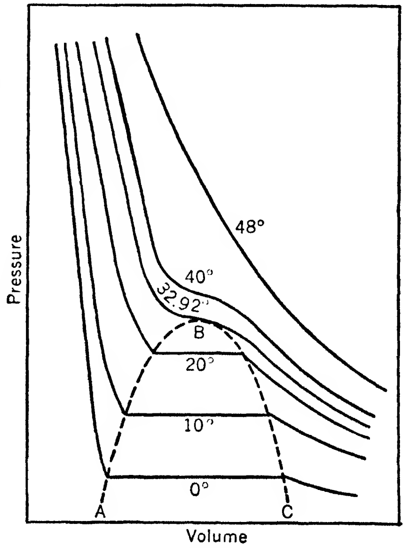

FIG. 1.—Isothermals for Carbon Dioxide

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[1] Andrews, *Trans. Roy. Soc.*, **159**, 583 (1869).

distance owing to an enormous shrinkage in volume caused by a small increase in pressure. At lower temperatures, the horizontal portions of the curves are much lower, indicating no pressure change during liquefaction. When all the gas has liquefied, the curves rise abruptly since there is only a small change in the volume of liquid for a large increase in pressure. At any point within the parabolic area *ABC* both vapor and liquid are coexistent; outside this area, only one form of matter, either vapor or liquid is present. Below the critical point there is a sharp transition from gas to liquid, but in reality the process may be a continuous one. We have already stated in our study of gases that van der Waals' equation applies to liquids as well as to gases, even at high pressures. This equation permits the construction of theoretical pressure-volume curves, and these curves have no sharp or sudden breaks such as appear in the actual discontinuous passage from the gaseous to the liquid state, thus indicating the continuity of the gaseous and liquid states.

If the values V, P, and T in van der Waals' equation be expressed as fractions of the corresponding critical values, and the values of the constants a, b, and R be substituted, we obtain an expression known as van der Waals' **reduced equation of state**:

$$\left(\alpha + \frac{3}{\beta^2}\right)(3\beta - 1) = 8\gamma$$

where α, β, and γ represent fractions of the critical values of P, V, and T, respectively. In this equation the individual nature of the substance does not appear and hence it may be applied to both gases and liquids, just as the fundamental gas equation can be applied to all gases regardless of their specific nature. However, it must be remembered that the reduced equation of state is only a rough approximation. It does, nevertheless, emphasize the fact that, unlike gases, liquids must be compared at their critical temperatures or at equal fractions of their critical temperatures, that is, in corresponding states. Many modifications of van der Waals' equation have been proposed from time to time, one of the more important being that of Berthelot (1899), in which a and b are expressed in terms of the critical constants. The most important application of the latter equation is in the precise determination of molecular weights by the vapor-density method, permitting calculating exact atomic weights.

Liquefaction of Gases. Faraday (1823) was one of the first workers to liquefy gases. He liquefied almost all the gases which condense under moderate pressures and at only moderately low temperatures. In 1895, machines for the liquefaction of large quantities of air were developed, independently, in Germany by Linde and in England by Hampson. Improvements on these machines were made by Dewar and Hampson. Claude has developed the most efficient apparatus for the liquefaction of air and other gases. It is based upon the regenerative principle, i.e., the energy of compression is conserved by passage of the expanding gases through an engine. In the Linde process the cooling is due entirely to the free expansion of the compressed gas. By means of the Claude apparatus all known gases have now been liquefied, the last and most difficult one being helium which was liquefied in 1908 by Kammerlingh Onnes in the cryogenic laboratory at Leyden.

The liquefaction of gases has become of great industrial importance. The fractional distillation of liquid air is the chief source of commercial oxygen and nitrogen. Solid carbon dioxide ("dry ice") is a new and important refrigerant. Ammonia, sulfur dioxide, and methyl chloride are extensively used in refrigeration machines. The separation of helium from natural gas on a commercial scale, by liquefaction, is one of the most brilliant achievements in American industry.

Heat of Vaporization. When a liquid is transformed into a vapor at the boiling-point much energy is required to overcome intermolecular attraction and some additional energy is used up in increasing the volume against the pressure of the atmosphere. This heat energy is not registered on the thermometer and is known as the **heat of vaporization** of the liquid. It is the heat required to convert one gram of a liquid, at its boiling-point, into vapor at the same temperature. The vaporization of one gram of water at 100° C. and under one atmosphere of pressure requires the expenditure of 538.7 cal. of heat energy. This value is called the heat of vaporization of water.

Trouton's Rule. In 1884 Trouton pointed out that the ratio of the molar heat of vaporization to the absolute boiling temperature of a liquid is constant, the numerical value of the ratio being 21 (approximately). Expressed as an equation,

$$\frac{M\mathrm{l}_v}{T} = 21$$

where M is the molecular weight of the liquid, 1_v the heat of vaporization of one gram, and T the absolute boiling-point. Nernst called attention to the fact that the constant varies with the temperature, and proposed two modified forms of the Trouton equation. Bingham has simplified the Nernst equations to the following form:

$$\frac{M1_v}{T} = 17 + 0.011T$$

Surface Tension. Liquids, like gases, are fluids and alter their shape to conform with that of the containing vessel. Unlike gases, they have a definite volume and need not completely fill the containing vessel. They offer great resistance to pressure and show a diminution in volume only at very high pressures. When the pressure is released they expand to their original volume but not beyond, except by passing into the vapor state. Therefore a liquid which does not fill the containing vessel exposes a "free surface" to its vapor, whereas the surface of a gas always coincides with that of the vessel containing it. At the surface of a liquid the molecules are pulled inward by the molecules below the surface, thus tending to reduce the surface area to a minimum. This makes the surface layer dense and hard to penetrate as if an elastic skin were drawn all about the liquid. The expansion of this surface layer or "skin" is resisted by a force which is known as **surface tension.** Surface tension explains many common phenomena: the toughness of soap bubbles, the spherical shape of raindrops, the way in which water insects are supported on the surface of water, the rise of water in a capillary tube, the movement of water in the soil or in blotting paper, etc.

Surface tension may be determined by several methods. A convenient method consists in measuring the height to which the liquid rises in a capillary tube. The equation employed is

$$\gamma = \frac{hdgr}{2 \cos \theta}$$

where γ is the surface tension, r the radius of the capillary tube, d the density of the liquid, h the height the liquid rises in the capillary tube, g the acceleration due to gravity, and θ the angle of contact of the liquid surface with the walls of the tube. θ for water and many other liquids is so small that it may be taken as zero, and thus $\cos \theta = 1$. The equation then becomes

$$\gamma = \tfrac{1}{2}hdgr$$

Hence, if the density and height to which a liquid rises in a previously calibrated capillary tube are known, the surface tension is readily calculated. When h and r are expressed in centimeters, the surface tension, γ, will be in dynes per centimeter or ergs per square centimeter.

Viscosity. Viscosity may be defined as the resistance offered or encountered by one portion of a liquid in moving over another portion. The law governing the flow of liquids through capillary tubes was discovered by Poiseuille in 1843. Liquids vary widely in viscosity; for example, ether is very mobile and tar is extremely viscous. In practice, the "relative viscosity" is usually determined, that is, the viscosity compared to that of a liquid of known viscosity taken as standard. Water is generally taken as the standard of reference and given a value of 1. The equation is

$$\frac{\eta_1}{1} = \frac{d_1 t_1}{d_w t_w}$$

in which η_1, d_1, and t_1 represent the viscosity, density, and time of flow through a capillary, respectively, of the liquid, and d_w and t_w the density and time of flow of water. To convert relative viscosities into absolute viscosities, it is necessary only to multiply their values by the absolute viscosity of water at the same temperature at which the relative viscosities were measured. It should be mentioned that fluidity, ϕ, is the reciprocal of viscosity, that is, $\phi = 1/\eta$. Obviously, fluidity is a measure of the tendency of a liquid to flow, whereas viscosity is a measure of the resistance to flow.

The measurement of viscosity or relative viscosity has many applications to various problems in both theoretical and applied chemistry, in biology, in physiology, and in many industries, including textile, paint, glue, rubber, etc.

Plasticity. According to Bancroft, "a material is plastic when permanent deformation involves no rupture and a break is self-healing." Bingham differentiates two types of flow: **viscous flow,**

such as, for example, is exhibited by particles of clay suspended in water when the concentration is low. At higher concentrations the clay particles stick together and require a definite minimum pressure to cause them to slip by each other. A flow of this type is called **plastic flow** and is exhibited by plastic solids. In other words, plastic flow requires an initial pressure to start it, whereas viscous flow requires no such initial impulse.

CHAPTER VIII

SOLIDS

The Kinetic Theory of Solids. Matter in the solid state differs from matter in the liquid and gaseous states chiefly in the fact that a solid has a definite form. A solid is rigid in structure, and its form cannot be altered greatly without fracture. This characteristic, however, is not universal, for some solids, graphite, for example, make ideal lubricants, and others, asbestos for example, may be formed into clothlike material. Glass, on the other hand, is very rigid, more so than many solids, and yet it is a liquid! Tar, pitch, waxes, and the like must be classified as liquids. Substances like these flow slowly, even at room temperature. When they are heated, they gradually become softer and softer and their rate of flow increases. They possess no true or sharp melting-point. True solids have a crystalline structure and show definite cleavage. The atoms are joined together in a regular geometric form called a **crystal lattice.** Moreover, when a pure crystalline solid is heated it remains rigid in structure until a certain temperature is reached, and then it passes rapidly into the liquid state with no further rise in temperature until all the solid has melted. This temperature is called the **melting-point** of the solid and is one of its distinguishing properties. In fact, determination of the melting-point of a solid is one of the most convenient ways of identification and is a determination frequently made by the organic chemist. In passing, it should be mentioned that some solids undergo a decomposition before a melting-point is reached.

Substances may be divided into two classes: **crystalline** and **amorphous.** Liquids, glassy solids, and the like are amorphous; that is, their constituent atoms are not arranged according to a definite pattern but are in a chaotic or haphazard arrangement. Certain substances owe their amorphous nature to a random arrangement of molecules or micelles; their atoms, however, show definite crystalline configurations.

According to the kinetic theory, the particles (atoms and groups of atoms) that compose solid substances are vibrating or rotating about **centers of rest** and do not glide over each other as they do in liquids or move independently and haphazardly as do gas particles. But undoubtedly some motion takes place in solids, as demonstrated by the diffusion of one metal into another. For example, a piece of tin after being in contact with lead for a long time (several years) will show the presence of a minute amount of lead. Furthermore, some solids (iodine, camphor, ice, etc.) continuously give off particles of vapor just as liquids do. This is known as **spontaneous evaporation** and is proof that the kinetic theory applies to solids as well as to liquids and gases. The particular state matter happens to be in is dependent upon the conditions of temperature and pressure. Eleven of the ninety known elements are gases: hydrogen, nitrogen, oxygen, fluorine, chlorine, and the six rare gases of the helium family. Bromine (non-metal), mercury (metal), cesium (metal, m.p. 28.5° C.), and gallium (metal, m.p. 29.75° C.) are liquids. All the other elements are solids.

Crystal Forms. The crystal form of a solid is a very important means of identification. There are a large number of crystalline forms, but all crystals may be classified into six systems based upon fundamental axes or degree of symmetry of the crystals. The six crystal systems are as follows:

1. *Regular (Isometric) System.* Crystals in this system are the most symmetrical figures of all. Some common forms are the octahedron (shown by alum), the cube (rock salt, for example), and the dodecahedron (frequently assumed by the garnet).

2. *Square Prismatic (Tetragonal) System.* This system includes crystals that are less symmetrical than those in the preceding system. In this system the crystals are lengthened in one direction. Examples: ordinary hydrated nickel sulfate, $NiSO_4 \cdot 6H_2O$, and the mineral zircon, $ZrSiO_4$.

3. *Hexagonal System.* Like the preceding system, this system frequently exhibits crystals that are elongated, but their section is a hexagon. Examples: calcite, $CaCO_3$, and quartz, SiO_2.

4. *Rhombic (Orthorhombic) System.* Crystals in this system have three unequal axes, all at right angles, and exhibit a good deal of symmetry. However, their section is always rhombic. Examples: topaz, sulfur, and potassium permanganate, $KMnO_4$.

5. *Monosymmetric (Monoclinic) System.* Crystals in this system have but one plane of symmetry. Examples: gypsum, $CaSO_4 \cdot 2H_2O$, feldspar, rock candy, tartaric acid, and potassium chlorate, $KClO_3$.

6. *Asymmetric (Triclinic) System.* This system includes crystals which have no plane of symmetry whatever. They have three axes, all unequal and inclined. Copper sulfate (blue vitriol), $CuSO_4 \cdot 5H_2O$, is a familiar example of the triclinic system.

The shapes of ornamental stones and "crystal" glass must not be confused with crystalline form. These are cut so as to cause them to reflect more light.

By dissolving impure crystals in a liquid and then allowing the dissolved substance to crystallize out on cooling the solution, or allowing it to evaporate, crystals of a higher degree of purity than the original ones are obtained. By repeating this process several times pure crystals are usually obtained. This process, called recrystallization, is the method most generally employed to purify solids. Crystallization also takes place when melted crystalline solids are allowed to cool to their respective melting-points or freezing-points. Crystals may be composed of elementary substances or of compounds.

Crystal Form and Chemical Composition. Although crystal form is an important means of identifying solid substances, there are many substances which may occur in several different crystal forms. This phenomenon is called polymorphism. Calcium carbonate crystallizes in two forms: as Iceland spar or calcite (in the hexagonal system) and as aragonite (in the rhombic system). Substances which crystallize in two forms are said to be **dimorphous.** The most important controlling factor in polymorphism is the temperature. The temperature at which one form changes into another is called the **transition temperature**; for example, sulfur crystallizes in the monoclinic system above 96.5° and in the rhombic form below this temperature.

In 1819, Mitscherlich discovered that when two substances crystallize in the same form with nearly identical angles, and can replace each other, they can usually be represented by similar chemical formulas. Such substances are said to be **isomorphous,** and the phenomenon was very useful in early atomic-weight determinations. It is known as **Mitscherlich's law of isomorphism** (see page 14).

X-Rays and Crystal Structure. X-rays are light waves of extremely short wave-length, approximately 1×10^{-8} cm. Since this is of the same order of magnitude as the distance between adjacent atoms in crystals, Laue (1912) suggested that the regularly arranged atoms of a crystal should act as a three-dimensional diffraction grating towards X-rays. Hence, by passing a pencil of X-rays through a crystal (thin section) and exposing a photographic plate behind the crystal and perpendicular to the path of the rays, the crystal pattern should be revealed on development. Friedrich and Knipping (1913) verified experimentally Laue's prediction. Two other methods of X-ray analysis have been developed and are of great value in studying crystalline substances. One is the method of Bragg and Bragg (father and son), who use the crystal as a reflection grating, rather than as a transmission grating, as in the Laue method. This method is much simpler than Laue's. A year or two after the Braggs announced their method, a modified method was devised almost simultaneously by Debye and Scherrer (1916) and by Hull (1917). Instead of rotating one large crystal as in the method of the Braggs, these investigators obtained the same results by using many small crystals orientated in all directions. This is called the "powder method."

The exact structures of many crystalline substances have been determined by X-ray analysis. Thus in inorganic compounds the individuality of molecules appears to have vanished and the ion seems to be the unit of structure. But in most organic compounds, the unit of structure is the molecule. In addition to its use in determining crystal structure, X-ray analysis has many practical applications in different fields, for example, in the examination of teeth, in the location of abnormal growths in the body, in the setting of bones, in many metallurgical operations, and in the examination of a great variety of materials, including substances not ordinarily classed as crystalline (e.g., asbestos, rubber, shellac, fibers, cellulose compounds, etc.).

Liquid Crystals. In 1888 Reinitzer discovered that cholesteryl acetate and cholesteryl benzoate when heated melt to turbid liquids at definite temperatures and on further heating they become clear at definite temperatures. On cooling these clear liquids, the reverse changes take place. An examination of these turbid liquids showed that they resembled ordinary liquids in their general behavior, but Lehmann discovered that they had optical properties which had hitherto been observed only with crystalline solids. Hence, he proposed that such liquids be called **liquid crystals,** the expression implying that the crystalline forces in these substances are so weak that the crystals easily undergo deformation and actually flow like liquids. Microscopic examination of these turbid liquids proved that they are not emulsions, the turbidity being due to the aggregation of a vast indefinite number of differently oriented transparent crystals. A fairly large number of examples of liquid crystals are now known.

CHAPTER IX

SOLUTIONS

So far we have been considering the behavior and properties of substances in the pure condition, i.e., pure gases, liquids, and solids. Let us now discuss mixtures of two or more pure substances. A solution may be defined as a chemically and physically homogeneous mixture of two or more pure substances. For example, if we add a few crystals of salt or sugar to water and stir thoroughly, we obtain a homogeneous mixture, or an aqueous solution of salt or sugar. If we mix alcohol and water or hydrogen sulfide gas and water, we obtain solutions of these substances. The salt, sugar, alcohol, and hydrogen sulfide are called **solutes** and the water is called the **solvent,** but these are purely relative terms used as a matter of convenience. The solute may be solid, liquid, or gaseous substances, and likewise, the solvent may be a solid, liquid, or a gas. Hence, there are nine kinds or classes of solutions, depending upon the state of the solute and solvent, respectively. They are as follows:

1. Solution of gas in gas.
2. Solution of liquid in gas.
3. Solution of solid in gas.
4. Solution of gas in liquid.
5. Solution of liquid in liquid.
6. Solution of solid in liquid.
7. Solution of gas in solid.
8. Solution of liquid in solid.
9. Solution of solid in solid.

Many examples of each of these different types of solutions are known. A solid dissolved in a liquid is the most common, but solutions of liquids in liquids and gases in liquids are also very common. Solutions of a gas in a gas are spoken of as gaseous mixtures, and solutions of a solid in a solid are called solid solutions, as for example, many of the alloys. When two liquids are miscible in all proportion, e.g., ethyl alcohol and water, they are said to be **consolute,** as either one may be regarded as the solvent (or solute).

Although a solution is homogeneous, its composition may be changed within certain limits, and this is the chief mark of distinction between a solution and a compound. The composition of a compound is also homogeneous, but it remains constant irrespective of changes in temperature and pressure.

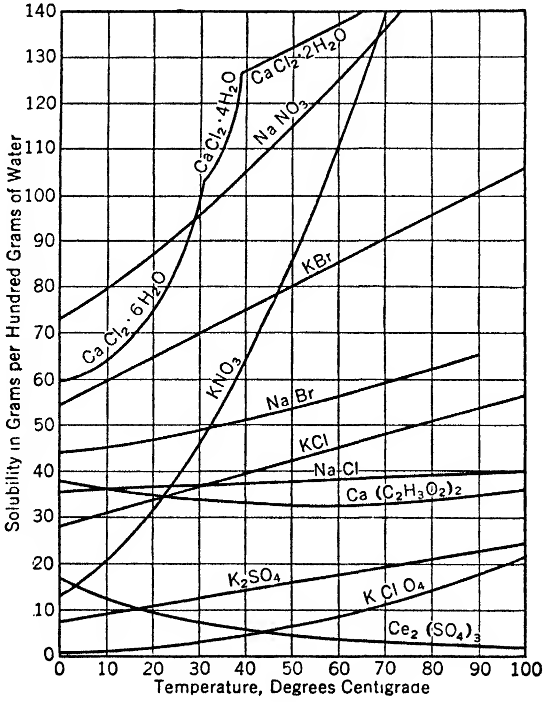

FIG. 2

The Extent of Solubility. All substances dissolve more or less, but if the amount that dissolves is very small in comparison to the solvent, the substance is said to be "insoluble." Barium sulfate, for example, is classed as an insoluble compound since a liter of water at 18° dissolves only 2.3 mg. On the other hand, many substances are highly soluble. One liter of water at 20° will dissolve 710 grams of magnesium sulfate, $MgSO_4 \cdot 7H_2O$, and certain solutes and solvents mix in all proportions. As a general rule, solid and liquid substances are more soluble at higher temperatures than at lower temperatures, but the reverse is true in some instances. The influence of temperature on the solubility of certain salts in water is shown in Fig. 2. The solubilities of some common salts and bases in water at 18° C. are given in the Table V.

TABLE V

SOLUBILITIES OF BASES AND SALTS IN WATER AT 18° *

	K	Na	Li	Ag	Tl	Ba	Sr	Ca	Mg	Zn	Pb
Cl	32.95 3.9	35.86 5.42	77.79 13.3	0.0_313 0.0_59	0.3 0.013	37.24 1.7	51.09 3.0	73.19 5.4	55.81 5.1	203.9 9.2	1.49 0.05
Br	65.86 4.6	88.76 6.9	168.7 12.6	0.0_41 0.0_66	0.042 0.0_215	103.6 2.9	96.52 3.4	143.3 5.2	103.1 4.6	478.2 9.8	0.598 0.02
I	137.5 6.0	177.9 8.1	161.5 8.5	0.0_635 0.0_71	0.006 0.0_317	201.4 3.8	169.2 3.9	200.0 4.8	148.2 4.1	419.0 6.9	0.08 0.0_22
F	92.56 12.4	4.44 1.06	0.27 0.11	195.4 13.5	72.05 3.0	0.16 0.0_292	0.012 0.001	0.0016 0.0_32	0.0087 0.0_214	0.005 0.0_35	0.06 0.002
NO_3	30.34 2.6	83.97 7.4	71.43 7.3	213.4 8.4	8.91 0.35	8.74 0.33	66.27 2.7	121.8 5.2	74.31 4.0	117.8 4.7	51.66 1.4
ClO_3	6.6 0.52	97.16 6.4	313.4 15.3	12.25 0.6	3.69 0.13	35.42 1.1	174.9 4.6	179.3 5.3	126.4 4.7	183.9 5.3	150.6 3.16
BrO_3	6.38 0.38	36.67 2.2	152.5 8.20	0.59 0.025	0.30 0.009	0.8 0.02	30.0 0.9	85.17 2.3	42.86 1.5	58.43 1.8	1.3 0.03
IO_3	7.62 0.35	8.33 0.4	80.43 3.84	0.004 0.0_314	0.059 0.0_216	0.05 0.001	0.25 0.0_257	0.25 0.007	6.87 0.26	0.83 0.02	0.002 0.0_43
OH	142.9 18.0	116.4 21.0	12.04 5.0	0.01 0.001	40.04 1.76	3.7 0.22	0.77 0.063	0.17 ✓ 0.02	0.001 0.0_32	0.0_35 0.0_45	0.01 0.0_34
SO_4	11.11 0.62	16.83 1.15	35.64 2.8	0.55 0.020	4.74 0.09	0.0_323 0.0_410	0.011 0.0_36	0.20 0.015	35.43 2.8	53.12 3.1	0.0041 0.0_313
CrO_4	63.1 2.7	61.21 3.30	111.6 6.5	0.0025 0.0_315	0.006 0.0_31	0.0_335 0.0_414	0.12 0.006	0.4 0.03	73.0 4.3	....	0.0_42 0.0_65
C_2O_4	30.27 1.6	3.34 0.24	7.22 0.69	0.0034 0.0_317	1.48 0.030	0.0085 0.0_338	0.0046 0.0_326	0.0_355 0.0_443	0.03 0.0027	0.0_364 0.0_44	0.0_316 0.0_554
CO_3	108.0 5.9	19.39 1.8	1.3 0.17	0.003 0.0_31	4.95 0.10	0.0023 0.0_311	0.0011 0.0_47	0.0013 0.0_313	0.1 ✓ 0.01	0.004? 0.0_33?	0.0_31 0.0_43

The *upper number* in each square gives the number of grams of the anhydrous salt held in solution by 100 c.c. of water. The *lower number* is the molar solubility, i.e., the number of moles contained in one liter of the saturated solution. The numbers for small solubilities have been abbreviated. Thus $0.0_64 = 0.0000004$

* Taken with permission from Smith's "Inorganic Chemistry," by Kendall. The Century Co., 1927.

Gases are usually less soluble at higher temperatures, and moreover, their solubility, unlike that of solids and liquids, is greatly influenced by pressure. **Henry's law** states that **the weight of a gas dissolved by a given volume of a liquid is directly proportional to the pressure of the gas.** In other words, the solubility of a gas is directly proportional to the concentration of gas molecules in the "free space" above the liquid. In a mixture of gases, each gas dissolves independently of the others (provided there is no chemical reaction) and in proportion to its **partial pressure.**

Can the Extent of Solubility Be Predicted? There is no general principle that will enable us to predict the extent of solubility of one substance in another, although it is true that solubility is to a large degree dependent upon similarity in character between solvent and solute. For example, a large number of organic compounds (e.g., solid hydrocarbons, fats, etc.) which are insoluble in water dissolve in ether or benzene with ease. Benzene is immiscible with water, but dissolves in its homologue, toluene, in all proportions. On the other hand, numerous inorganic compounds have a high solubility in water, notwithstanding the fact that they have little or no resemblance to it. In fact, inorganic compounds are usually more soluble in water than they are in organic solvents, such as alcohol, ether, benzene, etc. We stated in the preceding paragraph that no substance is absolutely insoluble. There is a wide difference in the extent of solubility of the numerous compounds, ranging from scarcely perceptible amounts up to very large ones. As yet these differences in solubility are unexplained. Sometimes we can predict qualitatively the solubility of compounds based upon a knowledge of the solubility of chemically related substances. For example, most salts of the alkali metals are very soluble in water. But similar chemical constitution is not the sole criterion; in fact, it is sometimes very misleading. For example, cellulose nitrate (guncotton) is soluble in a mixture of alcohol and ether, but not in these liquids separately. On the other hand, cellulose acetate, a similar compound, is soluble in these liquids separately, but not in the mixture! Again, calcium fluoride is "insoluble" in water, but the chloride, bromide, and iodide of calcium are quite soluble. Conversely, silver fluoride is extremely soluble in water, whereas the allied chloride, bromide, and iodide have very low solubilities.

Saturated Solutions and Supersaturated Solutions. When a solvent has dissolved all the solute it can at a given temperature and still be in equilibrium with an excess of the solute, the solution is said to be **saturated.** Under certain special conditions, a solution may be prepared which contains more solute than is present in a saturated solution. Such solutions are in a **metastable** condition and are called **supersaturated** solutions. See Fig. 3. By adding a small crystal of the solute to a supersaturated solution, crystallization begins at once and continues until equilibrium is attained, i.e., a saturated solution. This process is called "seeding." There are other ways of breaking up a supersaturated condition; for example, a sudden cooling of the solution, or vigorous shaking or stirring will generally start crystallization.

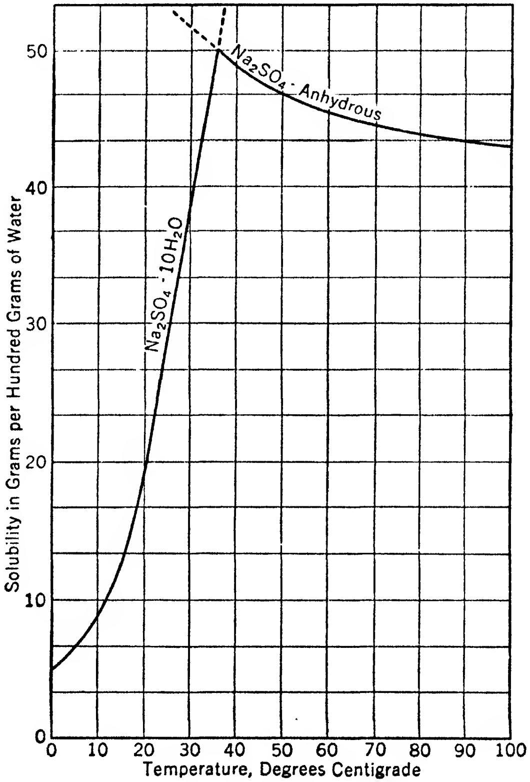

FIG. 3

Effect of Particle Size on Solubility. It has been shown by solubility determinations that the solubility of a slightly soluble substance increases as the size of the particles decreases. For example, Hulett[1] found that a saturated solution of gypsum at 25° C. contained 2.080 g. of $CaSO_4$ per liter. Upon adding very finely divided gypsum to this solution and shaking, the solubility increased to 2.542 g. of $CaSO_4$ per liter. Barium sulfate particles with an average diameter of 1.8 μ[2] have a solubility of 2.29 mg. per liter at 25° C. When this compound is ground in an agate mortar to a diameter of 0.1 μ, the solubility increases to 4.5 mg. per liter, which is almost double the solubility of the coarser particles. Similar results in a greater or lesser degree have been obtained with strontium sulfate, calcium fluoride, lead fluoride, lead iodide, silver chromate, and mercuric oxide. Upon allowing a solution saturated with an excess of very fine particles (supersaturated with respect to the coarser particles) to stand for a long time, the fine particles all disappear and the concentration of the solution decreases until it reaches the saturation value with respect to the coarser particles.

It seems very likely that this solubility phenomenon is a characteristic of all slightly soluble substances when they are in an extremely finely divided state. An explanation of the abnormally large solubility of very finely divided particles is to be found in the surface tension existing at the boundary surface between solids and liquids. This force tends to reduce the surface to its smallest possible value, and hence the smaller particles are converted into larger ones. Stated differently, the greater solubility of the very small particles may be due to the existence of more isolated atoms or groups of molecules which can break away from the solid surface more easily. This explanation seems plausible, since it is a fact that, when a mixture of large crystals and very small ones is allowed to stand, the small crystals become smaller and the large ones grow larger, until finally all the small crystals disappear. In other words, the large crystals grow at the expense of the smaller ones. This process is called "digesting," and it is commonly utilized in the analytical laboratory, since coarser particles are easier to filter and to wash. Moreover, if the particles of a precipitate are too finely divided they will pass through an ordinary paper filter. When a precipitate of a slightly soluble

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[1] Hulett, *Z. physik. Chem.*, **37**, 385 (1901); *J. Am. Chem. Soc.*, **27**, 49 (1905); see, also, Dundon and Mack, *J. Am. Chem. Soc.*, **45**, 2479 (1923); Dundon, *ibid.*, **45**, 2658 (1923).

[2] One micron (1 μ) = 0.001 mm.

substance, for example barium sulfate, is first formed, a mixture of different sizes of crystals is obtained—many extremely small, others relatively large. Hence, the solution is saturated with respect to the smaller crystals but **supersaturated** with respect to the larger ones. Therefore, in order for the solution to reach equilibrium with respect to the larger crystals, the smaller ones gradually disappear; that is, the solution becomes saturated with respect to the coarser crystals. The rate of digesting a precipitate can be increased by stirring and heating the mixture. Heating increases the solubility of the fine particles, and stirring brings fresh portions of the solution into contact with them, thus increasing the rate of diffusion whereby the dissolved particles are brought into contact with the surfaces of the coarse particles where deposition takes place.

Filtration and Washing of Precipitates. Beginners in analytical chemistry often ask the questions: How many washings of a precipitate are required? And how large a filter should be used?

In answer to the first question, it may be said that a precipitate should be washed until free from all soluble, non-volatile impurities. However, this point can never be reached because a portion of the solution always remains on the filter. But washing may be continued until the amount of dissolved substance remaining on the filter is so small that it may be disregarded, that is to say, it is so small that it cannot be detected by the analytical balance. This freeing the precipitate of soluble substances should be attained with as small a volume of wash liquid as possible. Since no precipitate is totally insoluble, it is obvious that the use of an excessively large volume of wash water may dissolve an appreciable amount of the precipitate. The volume of wash water or wash solution required depends largely upon the nature of the precipitate. Gelatinous or amorphous precipitates always require more washing than granular, crystalline precipitates, owing to the greater degree of adsorption by the former. In general, washing should be continued until foreign substances have been removed, as indicated by negative qualitative tests made on fresh, small portions of the filtrate. It is generally satisfactory to test frequently a fresh portion of the filtrate for some foreign ion known to be present in the original solution.

The most effective way to wash a precipitate is to use a number of small portions of the wash liquid, instead of the same total volume of liquid in fewer and larger portions.[3] The ideal relations follow a distribution law which may be expressed by the following equation:

$$X_n = \left(\frac{a}{m + a}\right)^n X_o$$

where X_o is the original concentration of impurity, X_n is the final concentration of impurity, n is the number of washings, m the number of milliliters used per washing, and a is the number of milliliters of liquid which remains with the precipitate after draining. In practice, the washing is never as effective as indicated by the theoretical equation.

The wash solution should be added in such a manner as to mix thoroughly with the precipitate and should be allowed to drain nearly completely before the next portion is added. Wash liquid is removed from precipitates much more efficiently by means of a centrifuge than by ordinary draining on a filter.

Often four or five washings (with ordinary drainage) are sufficient but sometimes from ten to twenty are required. Never wash a precipitate longer than is required to free it of impurities. To avoid excessive washing, make frequent tests on small, fresh portions of the filtrate.

As to the size of filter, it should always be selected with reference to the bulk of precipitate and never with respect to the volume of liquid to be filtered. The filter should not be so small that the precipitate occupies more than half its volume, and the wash liquid should never be added to a point higher than 5 or 6 mm. from the upper edge of the filter paper.

Problem. Suppose that the concentration of impurity in a solution in contact with a precipitate is $0.05M$, and that, upon filtering, one milliliter of liquid remains with the precipitate after each successive washing. Calculate the concentration of impurity remaining with the precipitate after washing with 50 ml. of liquid, when (1) two 25-ml. portions are used and (2) when five 10-ml. portions are employed. What is the theoretical ratio of impurities in the two cases?

Purifying Compounds by Recrystallization. Differences in solubilities are utilized in purifying solid compounds by the process

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[3] Ostwald, "Foundations of Analytical Chemistry" (translated by McGowan), third edition, p. 17, The Macmillan Co., New York, 1908.

of **recrystallization.** Usually three or four recrystallizations suffice to yield a compound of a high degree of purity. However, the recrystallized compound should always be tested to make certain that all impurities are absent, or at least all that would interfere with its use.

Solutions and the Kinetic Theory. The kinetic-molecular theory may be applied both to the process of solution and to the state of solution. For example, when a solid is placed in a liquid, the molecules leave the surface of the solid and produce the effect of a kind of pressure called the **solution pressure.** After leaving the solid, the molecules (or ions of electrolytes) move in all directions, and some return to the solid and attach themselves. The presence of the particles (molecules or ions) in the liquid produce what is called **diffusion** or **osmotic pressure.** When the number of particles returning to the solid is equal to the number leaving the solid in a given unit of time, the solution is in a state of equilibrium, i.e., it is **saturated.** In other words, equilibrium will have been reached when the diffusion (osmotic) pressure is equal to the solution pressure:

$$\text{Diffusion (osmotic) } P \rightleftarrows \text{Solution } P$$

Relation of Vapor Pressure and Boiling-Point. As the temperature of a liquid is raised, the average kinetic energy of the molecules becomes greater, and consequently there is a more rapid escape of molecules from the surface. In other words, the pressure of the vapor phase becomes higher as the temperature of a liquid is increased. When the vapor pressure of a liquid equals the pressure of the atmosphere above, bubbles of vapor form throughout the liquid and escape, i.e., the liquid boils. The **true boiling-point** of a liquid is the temperature at which its vapor pressure is equal to one atmosphere (760 mm. of mercury).

Vapor Pressure and Distillation. The vapor given off upon distilling a pure liquid has the same composition as the liquid. The vapor from mixed liquids usually contains the same components as the mixture, but not always in the same ratio. The vapor will be richer in the component having the higher vapor pressure, and the residue will boil at successively higher temperatures. For the sake of simplicity, only mixtures of two liquids (liquid pairs or binary mixtures) will be discussed. These may be divided into three general classes:

1. Completely immiscible liquids, i.e., insoluble.
2. Partially miscible liquids.
3. Completely miscible liquids.

1. With immiscible liquids, each exerts its own vapor pressure independent of the other, and the mixture boils when the sum of the two vapor pressures equals the atmospheric pressure. The vapor will contain the two components in the ratio of their vapor pressures, and hence the distillate will have a constant composition so long as both are present in the residue. Since the vapor pressure is constant, its curve is a horizontal line, as shown in Curve 1, Fig. 4. The well-known process of "steam distillation" is based upon this principle.

2. When two partially miscible liquids are mixed, each dissolves in the other to the respective saturation concentration and then any excess will cause the formation of two layers. Upon distillation, the mixture acts just like the immiscible liquids so long as two layers are present. The composition of the vapor is constant and depends upon the relative volatility of the two liquids. Just as soon as one layer is exhausted the vapor pressure falls off. See Curve 2, Fig. 4. An example of this class is a mixture of water and ethyl acetate.

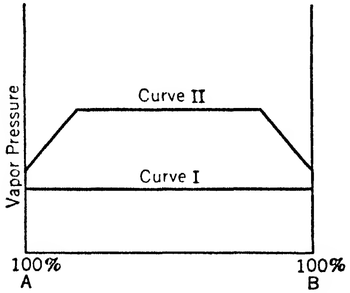

FIG. 4

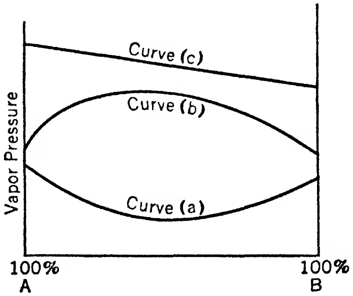

FIG. 5

3. The third class of liquid pairs, the completely miscible, includes three types. (*a*) When the vapor of either liquid is readily soluble in the other liquid, the vapor-pressure curve has a minimum and the boiling-point curve has a maximum. An example is a water solution of hydrogen chloride. See Curve (*a*), Fig. 5. (*b*) When the vapor of either liquid is only slightly soluble in the

other liquid, the vapor-pressure curve has a maximum and the boiling-point curve has a minimum. A mixture of water and ethyl alcohol is an example of this type of solution. See Curve (*b*), Fig. 5. (*c*) If the vapor of liquid *A* is readily soluble in liquid *B*, but the vapor of *B* is only slightly soluble in *A*, the vapor-pressure curve is a straight line as shown in Curve (*c*), Fig. 5. As the mixture distils, the liquid having the higher vapor pressure (lower boiling-point) comes over first, with gradually increasing amounts of the second liquid, until finally the less volatile (higher boiling-point) liquid is left. A mixture of water and methyl alcohol belongs to this type of solution.

Dilute Solutions and Osmotic Pressure. When a non-volatile solute is dissolved, the vapor pressure of the solvent is lowered. Hence, the boiling-point of the solvent is raised and the freezing-point is lowered. The dissolved molecules (or ions) of the solute diffuse about in solution very much in the same manner that gases diffuse. If this process of diffusion is hindered by a suitable partition (semi-permeable membrane), a pressure is developed. This pressure is called **osmotic pressure,** and the process by which it is developed is known as osmosis. The phenomenon of osmosis, like the freezing-point lowering and boiling-point elevation, is explained as involving the lowered vapor pressure of the solution. These phenomena are interrelated and form the basis for the determination of molecular weights and for the study of the properties of dissolved substances.

The lowering of the vapor pressure by a non-volatile solute may be explained by the kinetic theory applied to liquids, according to which vapor pressure is determined by an equilibrium between the evaporation of the liquid and the condensation of its vapor. The solute molecules will not prevent the return of the vapor molecules to the liquid, but may prevent molecules from escaping the liquid by occupying a portion of the free surface. Hence, equilibrium will be reached at a lower concentration of the vapor than with a pure solvent. This effect has been found to depend on the number of solute molecules and not on their nature.

In 1887, Raoult, a French chemist, discovered the fundamental law governing the vapor pressure of dilute solutions. This law states that **the ratio of the lowering of the vapor pressure to that of the pure solvent is equal to the ratio of the number of mols of solute to the total number of mols.**

Abbé Nollet (1748) discovered that certain animal membranes are permeable to water but not to sugar. Traube (1867) was the first to prepare artificial membranes, but Pfeffer (1877), a botanist, originated the idea of depositing the membrane in the walls of a porous cup and made the first quantitative measurements of osmotic pressure. He treated porous cups with potassium ferrocyanide and a cupric salt in such a way as partially to fill their pores with cupric ferrocyanide. In order to make an osmotic-pressure measurement, a mercury manometer is attached to the porous cup having the ferrocyanide membrane within its walls; the cup is then completely filled with the solution and sealed off. The apparatus is immersed in a bath of pure water kept at constant temperature, and after equilibrium has been established, the osmotic pressure is read off on the manometer. Make a sketch of an osmotic-pressure apparatus.

According to the kinetic theory, both osmotic pressure and gas pressure are due to molecular motion. Hence it would seem that the process of osmosis is very similar to the passage of hydrogen through palladium. In osmosis the solution is on one side of the semi-permeable membrane and the pure solvent on the other. Since the concentration of the solvent molecules is greater on the side where there is no solute, the solvent molecules will pass through the membrane, just as hydrogen passes through palladium, until their tendency to pass through the membrane is the same on both sides. The partial pressure of the solute will then be shown by the rise of the manometer.

Since Avogadro's law can be applied to dilute solutions as well as to gases, it is evident that osmotic-pressure measurements can be used as a means of determining molecular weights. One mol of a substance is the weight in grams which when dissolved in 22.4 liters of water at 0° exerts an osmotic pressure of one atmosphere. In practice, to avoid excessive deviations, much more dilute solutions are employed and the data calculated to one mol per 22.4 liters. Also, the direct measurement of osmotic pressure is not a practical method of molecular-weight determination, but there are simpler methods based upon osmotic-pressure relationships, for example, the boiling-point and freezing-point methods. A solute lowers the vapor pressure of a solvent and hence elevates its boiling-point and lowers its freezing-point. With non-ionizing organic compounds, such as sugar, glycerin, alcohol, urea, etc., each gram-mol of solute per 1000 g. of water elevates the boiling-point 0.52° (approximately) and lowers the freezing-point 1.86° (approximately), provided there is no reaction between the solute and the solvent. The 0.52° and 1.86° are called the **elevation constant** and the **depression constant,** respectively. Other solvents have different constants. Salts, acids, and bases produce similar effects but not by a constant amount and always to a greater extent than non-ionizing organic compounds. This abnormal elevation of the boiling-point and abnormal lowering of the freezing-point is due to **dissociation** (**ionization**) of the compounds.

As the principle of the above methods is the same, both are expressed mathematically by the following equation:

$$\Delta = \delta \times \frac{W \times 1000}{M \times g}$$

where Δ is the boiling-point elevation (or the freezing-point depression), δ the elevation (or depression) constant, W the weight of substance taken, M its molecular weight, and g the weight of solvent in grams. Rearranged, the equation is:

$$M = \frac{\delta W 1000}{\Delta g}$$

PROBLEMS

1. If 4.82 g. of cane sugar, $C_{12}H_{22}O_{11}$, are dissolved in 100 g. of water, (*a*) at what temperature will the solution freeze; (*b*) what is its boiling-point?

Ans. (*a*) −0.262° C.
(*b*) +100.073° C.

2. Calculate the freezing-point and the boiling-point of an aqueous solution containing 50 g. of glucose, $C_6H_{12}O_6$, per kilogram of water.

Ans. −0.516° C., +100.144° C.

3. If 4.60 g. of a certain organic compound are dissolved in 1000 g. of water and the temperature of the solution lowered to the freezing-point, which is observed to be −0.186° C., what is the molecular weight of the compound?

Ans. 46.

4. Calculate the molecular weight of a sugar, 17.1 g. of which dissolved in a kilogram of water depresses the freezing-point of the water 0.093° C.

Ans. 342.

5. What is the molecular weight of urea, if 6.01 g. of it dissolved in 500 g. of water form a solution which freezes at −0.373° C.?

Ans. 60.1.

6. What volume of ethanol (ethyl alcohol) must be added to 18 quarts of water in the radiator of an automobile in order to obtain an aqueous solution which freezes at 20° F.? The specific gravity of ethanol is 0.7893 $\frac{20^\circ}{4^\circ}$.

Ans. 3.6 qt.

7. A solution of 1.86 g. of glycerol in 100 g. of water boils at +100.105° C. under 1 atmosphere of pressure. Calculate the molecular weight of glycerol.

Ans. 92.

8. The solution resulting from dissolving 4.00 g. of a certain alcohol in 250 g. of water was found to boil at +100.26° C. (1 atmosphere). What is the molecular weight of the alcohol?

Ans. 32.

CHAPTER X

SOLUTIONS OF ELECTROLYTES

In the preceding chapter we dealt with solutions of all types of substances and regardless of whether solvent or solute was in the solid, liquid, or gaseous state. Experiment has shown that all chemical compounds may be divided into two classes depending upon their behavior in aqueous solution. For example, solutions of acids, bases, and salts conduct the electric current, while solutions of substances such as sugar, alcohol, glycerin, urea, etc., are non-conductors. Hence, the former type of compounds (in solution) are called **electrolytes** and the latter are called **non-electrolytes.** The line of distinction is not a sharp one, as some electrolytes form solutions that are poor conductors. Such substances are called weak electrolytes; the good conductors are called strong electrolytes. Note that the term **electrolyte,** strictly speaking, refers to **the solution of an ionized substance.** However, it is frequently applied to acids, bases, and salts because they form electrolytes when dissolved.

The acceptance of Avogadro's hypothesis was greatly retarded because experiment showed that certain substances have abnormal vapor densities. For example, ammonium chloride has a vapor density only about half that required for the formula NH_4Cl. On the other hand, the vapor density of acetic acid corresponds to a formula of higher molecular weight than that calculated from the formula $C_2H_4O_2$. The anomalous behavior of substances such as ammonium chloride has been shown to be due to a process called **dissociation,** and the abnormally high molecular weights found for compounds such as acetic acid have been ascribed to a process of aggregation of molecules known as **association.** Similar phenomena have been encountered upon extending the gas laws to dilute solutions, that is to say, the processes of association and dissociation may take place in solutions as well as in gases.

The Electrolytic Dissociation Theory. In 1887, Van't Hoff, a Dutch chemist, published in the first volume of the *Zeitschrift* *für physikalische Chemie* his great work on the analogy between solutions and gases. While engaged upon this work he discovered that solutions of most salts, those of all strong acids, and those of all strong bases seemed to act as exceptions to the general rule. For instance, their osmotic pressure was much greater for all concentrations than the gas pressure would be for corresponding concentrations and also was much greater than would be expected from the osmotic pressures of solutions of substances like sugar or urea at corresponding concentrations. These substances also caused too great a depression of the freezing-point and too great an elevation of the boiling-point of solutions. Van't Hoff saw the discrepancy and pointed it out clearly in his published paper. He then went on to say, "It may then have appeared daring to give Avogadro's law for solutions such a prominent place, and I should not have done so had not Arrhenius pointed out to me by letter the probability that salts and analogous substances when in solution **are split into ions.**" In this quotation we have the connecting link between the fundamental work of Van't Hoff and the theory of electrolytic dissociation which was enunciated by the Swedish chemist, Svante Arrhenius, in 1887. As a matter of fact, Arrhenius' paper [1] on his new theory of solutions of electrolytes appeared in the same volume of the *Zeitschrift für physikalische Chemie* as Van't Hoff's famous paper. Quoting from Arrhenius' paper: " If a gas shows such a deviation (referring to Van't Hoff's work) from the law of Avogadro it is explained by assuming that the gas is in a state of dissociation. The conduct of chlorine, bromine and iodine at higher temperatures is a very well-known example. The same expedient may, of course, be made use of to explain the exceptions to Van't Hoff's law; but it has not been put forward up to the present probably on account of the newness of the subject, the many exceptions known, and the vigorous objections which would be raised from the chemical side of such an explanation." Arrhenius then states his theory that only **electrolytes** are capable of undergoing ionic dissociation and shows how this explains all the exceptions to Van't Hoff's law. That is to say, osmotic pressure, freezing-point lowering, and boiling-point elevation are all **proportional to the number of particles present in a given volume of solution.** If a substance exerts an abnormally high osmotic pressure, causes an abnormally great freezing-point

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[1] *Z. physik. Chem.*, **1**, 631 (1887).

depression, and an abnormally high boiling-point elevation, then there must be more particles present than we would expect from the concentration. In other words, such substances must undergo a dissociation upon being dissolved, i.e., some of the molecules must break up into two or more particles. Arrhenius also pointed out that all substances which exhibit abnormal effects (acids, bases, and salts), when dissolved in water, yield solutions which conduct the electric current, whereas aqueous solutions which behave normally (e.g., sugar, alcohol, urea, etc.) do not conduct electricity any better than the pure solvent. He therefore divided substances (i.e., their solutions) into **electrolytes** and **non-electrolytes,** and called his hypothesis the "electrolytic dissociation theory," since only electrolytes can undergo **ionic dissociation.** The degree or per cent of ionization can be calculated from conductivity, freezing-point, and boiling-point measurements, and the values obtained by the three different methods are in very good agreement except for strong electrolytes. The anomaly of strong electrolytes is discussed on page 84. Table VI gives the percentage ionization of 0.1 normal solutions of some acids, bases, and salts at 18°.

Properties of Ionized Solutes. The chemical properties of an ion differ greatly from those of the corresponding atom or radical. For example, the potassium ion is present in an aqueous solution of potassium chloride, but there is no visible evidence that it reacts with the solvent; metallic potassium, on the other hand, reacts violently with water, liberating hydrogen and forming a solution of potassium hydroxide. In fact, the reaction is so vigorous that sufficient heat is generated to ignite the escaping hydrogen gas, which then burns with a beautiful violet-colored flame due to the presence of potassium vapor. Again, chlorine is a greenish-yellow gas, possessing a disagreeable odor, and is extremely irritating to the membranes of the nose and throat, producing coughing, inflammation, suffocation, and even death. But **chloride ion** is colorless, odorless, and harmless. Aqueous solutions of all chlorides react with solutions of all silver salts to yield insoluble silver chloride. This shows that in the process of solution chlorine and silver split off, or away, from the parent molecules and behave independently of all other particles present in the solution. On the other hand, chlorine in such compounds as chloroform ($CHCl_3$), carbon tetrachloride (CCl_4), etc., are not precipitated by silver nitrate, since they are not dissociated by water. Some chlorine compounds

TABLE VI

PERCENTAGE IONIZATION OF SOME ACIDS, BASES AND SALTS

(0.1 *N* solutions at 18° C.)

Compound	Ions	Percentage Ionization	Compound	Ions	Percentage Ionization
Acids			*Salts*		
HCl	H^+, Cl^-	92.0	KCl	K^+, Cl^-	86.0
HNO_3	H^+, NO_3^-	92.0	NaCl	Na^+, Cl^-	85.2
H_2SO_4	$2H^+, SO_4^{=}$	61.0	NH_4Cl	NH_4^+, Cl^-	85.3
$H_2C_2O_4$	$H^+, C_2O_4^{=}$	50.0	$NaCHO_2$	Na^+, CHO_2^-	85.4
H_3PO_4	$H^+, H_2PO_4^-$	27.0	$KC_2H_3O_2$	$K^+, C_2H_3O_2^-$	83.0
$HCHO_2$*	H^+, CHO_2^-	4.5	$NaC_2H_3O_2$	$Na^+, C_2H_3O_2$	77.9
$HC_2H_3O_2$	$H^+, C_2H_3O_2^-$	1.3	K_2SO_4	$2K^+, SO_4^{=}$	72.0
H_2CO_3	H^+, HCO_3^-	0.17	$ZnSO_4$	$Zn^{++}, SO_4^{=}$	40.0
H_2S	H^+, HS^-	0.07	$HgCl_2$	$Hg^{++}, 2Cl^-$	1.0
HCN	H^+, CN^-	0.01			
Bases			*Water*		
KOH	K^+, OH^-	91.0	H_2O	H^+, OH^-	0.0_614
NaOH	Na^+, OH^-	91.0			
$Ba(OH)_2$	$Ba^+, 2OH^-$	77.0			
NH_4OH	NH_4^+, OH^-	1.3			

*At 25° C.

which are dissociated by water do not exhibit reactions characteristic of the chloride ion, for example, potassium chlorate ($KClO_3$), which dissociates into potassium ions (K^+) and chlorate ions (ClO_3^-). In such compounds the chlorine is present in a complex ion. The above illustrations bring out the point that reactions between electrolytes in aqueous solution are between **ions, not molecules,** and is further proof that such substances undergo dissociation upon dissolving in water. Qualitative analysis is largely based upon the fact here illustrated.

The distinguishing properties of solutions of electrolytes may be summarized briefly as follows:

1. They conduct the electric current.
2. They exhibit abnormally high osmotic pressures.
3. They have abnormally low vapor pressures.

4. They have abnormally high boiling-points.
5. They have abnormally low freezing-points.
6. They exhibit characteristic chemical behavior.

All these properties may be accounted for, qualitatively at least, on the basis of the electrolytic dissociation (ionization) theory. In other words, the physical and the chemical properties of electrolytes are largely dependent upon the nature and concentration of the ions, thus distinguishing them from non-electrolytes, which do not ionize.

Interionic Attraction Theory. Although the electrolytic dissociation theory as originally stated was of great value in the study of solutions of electrolytes, it failed to account for the anomalous behavior of strong electrolytes. Experimental results on weak electrolytes in dilute solutions were in fairly good agreement with the theory. That is to say, the degree of dissociation, or per cent ionization, calculated from conductivity measurements appeared to be in agreement with the values obtained from osmotic phenomena. However, as improvement in experimental technique progressed and more exact data were accumulated, it became apparent that the Arrhenius theory was inadequate, especially when applied to strong electrolytes which have a high conductance. With the advent of X-ray analysis, it was revealed that crystals of such electrolytes as, for example, sodium chloride, are not built up of NaCl molecules but are composed of Na^+ ions and Cl^- ions arranged in a perfectly ordered fashion in what is termed a **space lattice** or **ionic lattice.** Hence, it appeared logical to assume that dilute solutions of such compounds contain no molecules, since there are none in their crystals. From this it follows that salts, and strong acids and bases, may be considered as completely ionized in solution, and hence the degree of dissociation as calculated according to the Arrhenius theory loses its significance for electrolytes of this type. Moreover, the molal freezing-point depressions should be exact multiples of the constant $-1.86°$ from infinite dilution up to moderate concentrations. For example, KCl should give exactly twice the normal depression. Freezing-point experiments show that KCl gives less than twice the normal depression and that the molal depression decreases as the concentration increases! The Debye and Hückel (1923) **interionic attraction theory** offers an explanation. According to this theory, the oppositely charged ions attract each other and cause deviations from the ideal solution, just as the attraction between gas molecules (represented by a in the van der Waals' equation) causes deviations from the ideal gas. At low concentrations the electrolytes approach the ideal solution since their ions are so far apart that interionic attraction is negligible. Similarly, imperfect gases at low pressures approach the ideal gas in their behavior. The Debye and Hückel theory is very satisfactory from a theoretical standpoint and agrees well with the experimental facts of electrical conductance and osmotic properties of dilute solutions of strong electrolytes. No satisfactory theory has been developed for concentrated solutions of strong electrolytes.

In passing, it should be mentioned that other factors besides the attraction of oppositely charged ions cause deviations from the laws of ideal solutions, such as the hydration of molecules and of ions, etc. Moreover, pending the determination of true ionic concentrations by methods yet to be discovered, we make use of the approximate ionic concentrations obtained from measurements of conductance, freezing-point lowering, etc.

CHAPTER XI

HOMOGENEOUS EQUILIBRIUM

The Law of Mass Action. Guldberg and Waage, two Norwegian chemists, showed experimentally in 1867 that **the rate, or speed, of a chemical reaction is proportional to the active masses of each of the reacting substances.** This is known as the **law of mass action.** By "active masses" is meant the molecular concentrations of the substances reacting.

Suppose we consider a reversible reaction in which substances A and B react to form substances C and D:

$$A + B \rightleftharpoons C + D$$

Let the molar concentrations of the substances be represented by C_A, C_B, C_C, and C_D. By experiment it has been shown that S_1, the speed at which A and B react to form C and D, is directly proportional to the concentration of A and also to the concentration of B. Hence, S_1 is also proportional to the product of the concentrations of A and B, thus

$$S_1 = C_A \times C_B \times k_1 \tag{1}$$

where k_1 is the proportionality constant. Equation (1) is an algebraic statement of the law of mass action. When more than one mol of a given substance takes part in a reaction, then its concentration must be raised to a power equal to the number of mols reacting. For example, if there are m mols of A and n mols of B, then the mass law equation becomes:

$$S_1 = C_A^m \times C_B^n \times k_1.$$

Similarly, S_2, the speed at which C and D react to form A and B, is proportional to the concentrations of C and D and therefore is proportional to their product. Hence,

$$S_2 = C_C \times C_D \times k_2 \tag{2}$$

where k_2 is the proportionality constant for the reverse reaction. If p mols of C are formed and q mols of D, then the mass law equation for the reverse reaction is written:

$$S_2 = C_C^p \times C_D^q \times k_2.$$

At the beginning of the reaction A and B will have their highest concentrations and hence S_1 will be at its maximum value. But as A and B react to form C and D their concentrations diminish and hence S_1 diminishes. On the other hand, S_2 at the start will be zero but it will increase as the concentrations of C and D become greater. In other words, S_1 decreases progressively as S_2 increases. Finally, the two velocities become equal. This is called the **equilibrium point.**

$$S_1 = S_2 \tag{3}$$

Substituting (1) and (2)

$$C_A \times C_B \times k_1 = C_C \times C_D \times k_2 \tag{4}$$

or

$$\frac{C_C \times C_D}{C_A \times C_B} = \frac{k_1}{k_2} = K \tag{5}$$

K is called the **equilibrium constant.** Its magnitude changes with changes in temperature, but it is a constant value at any given temperature and is a measure of chemical affinity, that is, a measure of the extent to which the reactants react to give the products.

If two substances react reversibly to form three other substances, for example,

$$A + B \rightleftharpoons C + D + E$$

the equilibrium equation is

$$\frac{C_C \times C_D \times C_E}{C_A \times C_B} = K \tag{6}$$

Or suppose that two or more mols of some or each of the substances enter into the reaction, as for example,

$$A + 2B \rightleftharpoons 3C + D$$

Then the equilibrium equation is

$$\frac{C_C^3 \times C_D}{C_A \times C_B^2} = K \tag{7}$$

As stated above, in such reactions each concentration must be raised to a power equal to the number of mols entering into the reaction. In general,

$$mA + nB \rightleftharpoons pC + qD$$

and the equation for the equilibrium is written

$$\frac{C_C^p \times C_D^q}{C_A^m \times C_B^n} = K \tag{8}$$

Equation (8) is a general expression of the **law of chemical equilibrium,** one of the most important chemical principles. This law states that **at a given temperature, equilibrium is reached in a reversible reaction, when the product of the concentrations of the substances formed, divided by the product of the concentrations of the substances reacting (each concentration raised to a power equal to the number of mols reacting), is a constant.** It should be mentioned that it is purely a matter of convention that the product of the concentrations of the substances formed is divided by the product of the concentrations of the reacting substances. The reciprocal ratio would also be constant, but of course its value for K would be the reciprocal of the former value.

The law of chemical equilibrium holds only approximately with ordinary substances when concentrations or pressures are used. In order to employ this law with precision, G. N. Lewis introduced corrected terms which he called **activities** and **fugacities.** Activities have the dimensions of concentrations and are really the "effective" concentrations, involving the behavior of both solute and solvent. Fugacity has the dimensions of pressure and is in fact a corrected pressure which the real gas would have if it could be converted into an ideal, or perfect, gas. Activities and fugacities are determined by experiment, and for exact calculations these must be employed instead of concentrations and pressures.

Equilibria in Solutions of Electrolytes. The mass law, or law of chemical equilibrium, has a wide application to all reversible reactions or systems: for example, the distribution of a solute between two immiscible solvents; reactions between molecules of organic compounds; molecular gas reactions; and ionic reactions, including simple ionization equilibria, complex ion equilibria, hydrolysis, equilibria of ions of precipitates, and oxidation-reduction equilibria. Only its application to certain types of ionic equilibria will be dealt with here.

Since the ionization of electrolytes in solution is a reversible process, we would expect that their equilibria could be expressed quantitatively by the mass law. However, this is true only of dilute solutions of weak electrolytes such as ammonium hydroxide and acetic acid, for example. The law of mass action cannot be applied to solutions of strong electrolytes like sodium hydroxide, hydrochloric acid, and sodium chloride, as experiment shows that the value for K does not remain constant, but increases with increasing concentration of the solution. This means that, as the concentration increases, the percentage ionization decreases too slowly to obey the law of mass action. Various explanations of this abnormality of strong electrolytes have been proposed. For example, all ions are probably hydrated in solution and hence the speed of the ions would not remain constant.

In 1923, Debye and Hückel developed a mass law equation that has proved very satisfactory for dilute solutions of strong electrolytes but it will not hold for their concentrated solutions. This equation is based upon forces of attraction between the ions (see page 84). In weak electrolytes the electrical forces between the ions are negligible because the ions are comparatively few in number and hence are far apart. But in strong electrolytes which are completely ionized, the concentration of the ions is so great that the interionic attraction becomes very pronounced and thus the velocity of the ions is reduced. Hence, the equivalent conductance of the solution is less than it would be if the ionic velocity had not been reduced. In other words, the attractive force between the ions has the same effect upon the conductance as incomplete ionization.

Ostwald's Dilution Law. In the preceding paragraphs it was pointed out that the mass law is applicable not only to chemical equilibria in both liquid and gaseous systems but also to electrolytic equilibria, i.e., solutions of weak acids and bases. For example, when acetic acid is dissolved in water it dissociates into hydrogen ions and acetate ions as represented by the following equation:

$$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$$

Suppose that one mol of acetic acid is dissolved in water and diluted to v liters. Let α equal the degree of dissociation. The concentration of each ion is then α/v, and that of the un-ionized acid is $(1 - \alpha)/v$. The equilibrium or ionization constant, K, may then be written as follows:

$$K = \frac{C_{H^+} \times C_{CH_3COO^-}}{C_{CH_3COOH}} = \frac{\alpha/v \times \alpha/v}{\frac{1-\alpha}{v}} = \frac{\alpha^2}{(1-\alpha)v}$$

This equation, which expresses the relation between the degree of ionization and dilution, was first developed by Ostwald and is called the **Ostwald dilution law.**

The Common-Ion Effect. Upon adding to a solution of a weak electrolyte some strong electrolyte having one ion in common, the ionization of the weak electrolyte is repressed until equilibrium is re-established. This is called the common-ion effect, and it is frequently employed in analytical procedures in regulating hydrogen- or hydroxyl-ion concentration, or to decrease the solubility of a slightly soluble substance. For example, if ammonium acetate be added to an acetic acid solution, the net effect will be a lowering of the hydrogen-ion concentration. Similarly, if ammonium chloride be added to a solution of ammonium hydroxide, the hydroxyl-ion concentration will be lowered.

Buffer Solutions. Pure water has a hydrogen-ion (also hydroxyl-ion) concentration of 1×10^{-7} equivalent per liter. A single drop of a normal acid added to a liter of pure water will greatly increase the hydrogen-ion concentration. Likewise a single drop of a normal base will greatly increase the hydroxyl-ion concentration of the water. Hence, pure water has no reserve neutralizing power to prevent the change of its H^+/OH^- ratio. However, experiment has shown that any solution containing a weak acid and one of its salts, or a weak base and one of its salts, can neutralize both acids and bases, within certain limits; i.e., it can keep its H^+/OH^- ratio constant (or approximately constant). Such solutions are called **buffer solutions,** and their resistance to hydrogen-ion change is known as **buffer action.** The common-ion effect is the basis of buffer action. Buffer solutions are extensively used in determining *p*H by the colorimetric method, and buffer action plays an important rôle in maintaining the proper H^+/OH^- ratio in many chemical processes. A more detailed discussion of this subject is given on pages 197–201.

CHAPTER XII

HETEROGENEOUS EQUILIBRIUM

In the preceding pages we discussed equilibria between substances mixed in a homogeneous fashion, such as a mixture of gases or substances dissolved in a liquid. When substances are separated from one another by distinct boundary lines, as for example, a liquid and its vapor, a solid and a liquid, or a solid and a gas, the mixtures are heterogeneous. Equilibria in such systems are called heterogeneous equilibria, but the factors governing them are the same as those which govern homogeneous equilibria, namely, concentration, temperature, and pressure.

The following are some examples of heterogeneous equilibria: (*a*) a liquid in equilibrium with its vapor: e.g., $H_2O(l) \rightleftharpoons H_2O(g)$; (*b*) a solid in equilibrium with its products of dissociation: e.g., $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$; (*c*) a solid in equilibrium with its saturated solution, and vapor: e.g., $NaCl(s) \rightleftharpoons \underset{\text{Sat. aq. soln.}}{NaCl} + H_2O(g)$.

The Law of Partition. When a solute is added to a mixture of two immiscible solvents at a constant temperature, the ratio in which it distributes itself between the solvents is constant, provided the molecular weight of the solute is the same in both solvents. This is known as Nernst's distribution law. The ratio in which a solute distributes itself between two non-miscible solvents is called the **partition coefficient** or **distribution coefficient.** This principle of partition is extensively used in the organic laboratory in extraction processes.

The Phase Rule. After studying many cases of heterogeneous equilibria, Willard Gibbs (1876), a mathematical physicist at Yale University, developed a system of classification which is now commonly known as the **phase rule.** As his principle was stated in terms of abstract mathematics, it was not until 1887, when Roozeboom simplified the mathematics, that the phase rule was made available to the general worker in the solution of chemical problems. A simple statement of the phase rule is:

$$F = C - P + 2$$

P is the number of **phases,** i.e., the number of separate physical states which can exist in a system at equilibrium. The physical states are solid, liquid, and gas. C is the number of **components,** i.e., the number of independent chemical substances which are required to build up the system. F is the number of **degrees of freedom,** i.e., the number of independent variables (concentrations, temperature, and pressure) which may be altered at once without destroying any phase. Two illustrations are as follows:

1. A mixture of ice, water, and vapor. This system has one component (H_2O) and three phases. $\therefore F = 0$. The system is non-variant.

2. The dissociation of calcium carbonate.

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

There are two components (CaO and CO_2) and three phases (two solid and one gas). $\therefore F = 1$. The system is monovariant.

The phase rule has proved very valuable in determining the presence or absence of allotropic forms of compounds, in determining whether a compound or a solution is formed, in the study of alloys, and in many other practical problems such as the extraction of certain salts from salt deposits.

The Solubility-Product Principle. Originally the solubility-product principle was based upon the application of the law of mass action to two equilibria. In the first place, it was assumed that the concentration of undissociated molecules in a solution of a slightly soluble salt is proportional to the "active mass" of the solid; i.e., that the undissociated molecules have a definite solubility. Secondly, the law of mass action was applied to the equilibrium between the undissociated molecules and their ions. For example, consider a slightly soluble salt BA in equilibrium with its saturated solution:

$$BA(s) \rightleftharpoons BA \rightleftharpoons B^+ + A^-$$

Denoting concentrations by C, we have

$$C_{BA} = k_1 C_{BA(s)} \qquad (1)$$

$$\frac{C_{B^+} \times C_{A^-}}{C_{BA}} = k_2 \tag{2}$$

Therefore,

$$C_{B^+} \times C_{A^-} = K \tag{3}$$

where K is the solubility-product constant.

Both the above applications are now known to be incorrect. A. A. Noyes and others [1] proved that the concentration of undissociated salt (as determined by conductivity measurements) is not constant. And almost from the first it was realized that the law of mass action cannot be applied to the equilibrium between a salt and its ions. More recently Butler [2] has presented a simple deduction of the solubility product equation based upon his more elaborate statistical treatment published in the *Journal of Physical Chemistry*, **28**, 438–448 (1924):

> It assumes that the ions of a simple salt take part independently in the process of solution at the crystal surface. Modern knowledge makes this conception inevitable. If the salt is almost or entirely dissociated into ions in solution, and if the solid crystal is rightly regarded as a lattice structure built up of positive and negative ions, there is no reason to postulate the appearance of the molecule at any stage in the process of solution.
>
> An ion leaves the surface and passes into solution when it has acquired by thermal agitation sufficient energy to carry it out of the range of the attractive forces at the crystal surface. An ion becomes deposited when it reaches the surface from solution at a place at which it can become permanently attached. In the simplest case of a cubic lattice a positive ion must be deposited above a negative one and *vice versa*, in order to continue the crystal lattice. It follows that the rate at which an ion leaves the surface is proportional in the first place to the number in the surface layer, whilst the rate of deposition of an ion is proportional to its concentration in solution and to the number of places at the surface at which it can become attached. Equilibrium is attained when equal numbers of both kinds of ions are dissolved and deposited in the same time.
>
> Now consider the state of the crystal surface in contact with the solution. Take the case of a crystal normally containing equal numbers of positive and negative ions in its surface layer. In contact with solution there may be a greater tendency for the one ion to leave or to become deposited at the surface than the other.

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[1] *J. Am. Chem. Soc.*, 1911, et seq.

[2] *J. Soc. Chem. Ind.*, **43**, 634–635 (1924).

The facility with which precipitates of insoluble salts adsorb a common ion is well known. Fajans and Frankenburger [*Z. physik. Chem.*, **105**, 255 (1923)] have recently determined the amount of silver ion adsorbed by silver bromide crystals and found for one particular dilute solution an adsorption of one silver ion for every four to ten bromide ions of the exposed surface.

The result may be roughly illustrated as follows: I shows a cross-section of the two layers next to the surface of a complete crystal; II the same for a crystal with an incomplete surface layer which has lost more positive than negative ions.

I

$$\begin{array}{cccccccccc} - & + & - & + & - & + & - & + & - & + \\ + & - & + & - & + & - & + & - & + & - \end{array}$$

Exposed, 5 +, 5 −.

II

$$\begin{array}{cccccccccc} - & + & - & & - & & - & + & - & + \\ + & - & + & - & + & - & + & - & + & - \end{array}$$

Exposed, 3 +, 7 −.

It is evident that the loss of a positive ion exposes a negative ion and *vice versa.*

Suppose that at equilibrium Nx positive ions and $N(1 - x)$ negative ions are exposed at the surface. Then we can write the following proportionalities:

Rate of solution of positive ions $= k_1Nx$
Rate of deposition of positive ions $= k_2N(1 - x)C_1$
Rate of solution of negative ions $= k_3N(1 - x)$
Rate of deposition of negative ions $= k_4NxC_2$

where C_1 and C_2 are the concentrations of the positive and negative ions in solution.

For equilibrium

$$k_1Nx = k_2N(1 - x)C_1$$

and

$$k_3N(1 - x) = k_4NxC_2$$

whence

$$C_1 \times C_2 = \frac{k_1k_3}{k_2k_4} = K$$

which is the law of the solubility product.

This equation states that, in a solution containing ions which by their union form a slightly soluble compound, the ions will be in equilibrium when the product of their gram-ion concentrations attains a certain definite value, each concentration being raised to a power equal to the relative number of gram-ions derived from the ionization of one mol of the original compound. The numerical value of this product is called the solubility-product constant, K, often written $K_{\text{s.p.}}$. This is a special equilibrium constant which expresses the relation between ions in equilibrium with a saturated solution of their salt. It is evident that if the addition of electrolytes, whether they contain a common ion or not, causes any change in the conditions of solution (e.g., by affecting the attraction of either the solvent or the solid solute for the ions), the values of k_1, k_2, etc., will not remain constant, i.e., $K_{\text{s.p.}}$ will not be constant. At best the solubility-product equation is merely an approximation and holds rigorously only for solutions of very slightly soluble electrolytes and in solutions of the pure salt. The numerical value of $K_{\text{s.p.}}$ is different for each compound and varies slightly with the temperature for the same compound. For temperatures between 15° and 35° the variation is so small that for most slightly soluble compounds the value for $K_{\text{s.p.}}$ may be regarded as independent of the temperature.

Let us apply the solubility-product principle, as above deduced, to a slightly soluble salt of the BA type. Silver chloride may be taken as an example. In its saturated solution containing an excess of the solid phase an equilibrium exists between the speed at which the solid dissolves and that at which solid forms:

$$\underset{\text{Solid}}{\text{AgCl}} \rightleftharpoons \text{Ag}^+ + \text{Cl}^-$$

Consider the solid surface as a lattice, and let

x = the portion containing Ag^+ ions;
$1 - x$ = the remaining surface which contains Cl^- ions;
k_1x = the speed at which Ag^+ ions leave the surface, k_1 being a proportionality factor (a speed constant);
$k_2(1-x)C_{\text{Ag}^+}$ = the speed at which Ag^+ ions deposit on the surface.

At equilibrium,

$$K_1x = k_2(1 - x)C_{\mathrm{Ag}^+} \tag{1}$$

Likewise,

$k_3(1 - x)$ = the speed at which Cl^- ions pass into solution.
$k_4 \times C_{\mathrm{Cl}^-}$ = the speed at which Cl^- ions deposit on the surface.

At equilibrium,

$$k_3(1 - x) = k_4 \times C_{\mathrm{Cl}^-} \tag{2}$$

From equation (1)

$$C_{\mathrm{Ag}^+} = \frac{k_1x}{k_2(1 - x)}$$

and from (2)

$$C_{\mathrm{Cl}^-} = \frac{k_3(1 - x)}{k_4x}$$

Combining (1) and (2) we have for the combined action of the Ag^+ and Cl^- ions,

$$C_{\mathrm{Ag}^+} \times C_{\mathrm{Cl}^-} = \frac{k_1k_3}{k_2k_4} = K_{\mathrm{s.p}}$$

This expression states that, when the product of the gram-ion concentrations of Ag^+ and Cl^- ions attains the value for $K_{\mathrm{s.p.}}$, the solution is saturated with respect to these ions. Note that the equation contains no numerical or other factor representing the amount of solid AgCl which may be present. This is as it should be, since the **excess** solid, however large or small, has no influence on the concentration of the ions in its saturated solution. In other words, the solubility of a pure compound in a pure solvent has a definite and constant value at a given temperature. Such a condition seldom, if ever, exists in analytical procedures, and hence the solubility-product equation is only an approximation.

Each compound of the types BA_2 and B_2A yields on ionization two similar ions and one dissimilar ion. Their solubility-product expressions are:

$$C_{B^+} \times C^2_{A^-} = K_{\text{s.p.}}(BA_2)$$

and

$$C^2_{B^+} \times C_{A^-} = K_{\text{s.p.}}(B_2A)$$

Examples of slightly soluble compounds of the BA_2 type are: $PbCl_2$, $Mg(OH)_2$, and CaF_2. The B_2A type is illustrated by Ag_2SO_4 and Ag_2S.

For compounds of the types BA_3 and B_3A the solubility-product equations are:

$$C_{B^+} \times C^3_{A^-} = K_{\text{s.p.}(BA_3)}$$

and

$$C^3_{B^+} \times C_{A^-} = K_{\text{s.p.}(B_3A)}$$

Examples are $Al(OH)_3$, $Fe(OH)_3$, and Ag_3PO_4.

For a mixed salt like $MgNH_4PO_4$ the solubility product equation is

$$C_{\text{Mg}^{++}} \times C_{\text{NH}_4^+} \times C_{\text{PO}_4^{\equiv}} = K_{\text{s.p.}(\text{MgNH}_4\text{PO}_4)}$$

In general, for a slightly soluble salt B_mA_n, we would have, as the relative number of ions which it would yield upon ionizing, m cations and n anions according to the scheme:

$$\underset{\text{(Solid)}}{B_mA_n} \rightleftharpoons B_m{}^{+\cdots} + A_n{}^{-\cdots}$$

The solubility-product equation would be

$$C^m_{B^{+\cdots}} \times C^n_{A^{-\cdots}} = K_{\text{s.p.}(B_mA_n)}$$

in which $C_{B^{+\cdots}}$ is the total concentration of the $B^{+\cdots}$ ions, whose value must be raised to the mth power, and $C_{A^{-\cdots}}$ is the total concentration of the $A^{-\cdots}$ ions, whose value must be raised to the nth power.

Problems involving applications of the solubility-product principle will be treated in Chapter XV. The values of the solubility-product constants of the slightly soluble compounds frequently encountered in qualitative analysis are given in Table VII.

TABLE VII

SOLUBILITY PRODUCTS

Compound	Ions	$K_{\mathrm{s.p.}}$*
Acid tartrate		
Potassium	$C_{\mathrm{K}^+} \times C_{[\mathrm{HC_4H_4O_6}]^-}$	3.8×10^{-4}
Bichromate		
Silver	$C^2_{\mathrm{Ag}^+} \times C_{\mathrm{Cr_2O_7}^=}$	2×10^{-7}
Bromates		
Silver	$C_{\mathrm{Ag}^+} \times C_{\mathrm{BrO_3}^-}$	5×10^{-5}
Thallous	$C_{\mathrm{Tl}^+} \times C_{\mathrm{BrO_3}^-}$	8.5×10^{-5}
Bromides		
Cuprous	$C_{\mathrm{Cu}^+} \times C_{\mathrm{Br}^-}$	4.1×10^{-8}
Lead	$C_{\mathrm{Pb}^{++}} \times C^2_{\mathrm{Br}^-}$	7.9×10^{-5}
Mercurous	$C_{\mathrm{Hg_2}^{++}} \times C^2_{\mathrm{Br}^-}$	1.3×10^{-21}
Silver	$C_{\mathrm{Ag}^+} \times C_{\mathrm{Br}^-}$	4.0×10^{-13}
Thallous	$C_{\mathrm{Tl}^+} \times C_{\mathrm{Br}^-}$	2.9×10^{-6}
Carbonates		
Barium	$C_{\mathrm{Ba}^{++}} \times C_{\mathrm{CO_3}^=}$	8.1×10^{-9}
Calcium	$C_{\mathrm{Ca}^{++}} \times C_{\mathrm{CO_3}^=}$	1.2×10^{-8}
Lead	$C_{\mathrm{Pb}^{++}} \times C_{\mathrm{CO_3}^=}$	3.3×10^{-14}
Magnesium	$C_{\mathrm{Mg}^{++}} \times C_{\mathrm{CO_3}^=}$	2×10^{-4}
Silver	$C^2_{\mathrm{Ag}^+} \times C_{\mathrm{CO_3}^=}$	6.1×10^{-12}
Strontium	$C_{\mathrm{Sr}^{++}} \times C_{\mathrm{CO_3}^=}$	1.6×10^{-9}
Chlorides		
Cuprous	$C_{\mathrm{Cu}^+} \times C_{\mathrm{Cl}^-}$	1.0×10^{-6}
Lead	$C_{\mathrm{Pb}^{++}} \times C^2_{\mathrm{Cl}^-}$	2.4×10^{-4}
Mercurous	$C_{\mathrm{Hg_2}^{++}} \times C^2_{\mathrm{Cl}^-}$	2.1×10^{-18}
Silver	$C_{\mathrm{Ag}^+} \times C_{\mathrm{Cl}^-}$	1.1×10^{-10}
Thallous	$C_{\mathrm{Tl}^+} \times C_{\mathrm{Cl}^-}$	2.0×10^{-4}
Chloroplatinate		
Potassium	$C^2_{\mathrm{K}^+} \times C_{[\mathrm{PtCl_6}]^=}$	4.9×10^{-5}
Chromates		
Barium	$C_{\mathrm{Ba}^{++}} \times C_{\mathrm{CrO_4}^=}$	2.3×10^{-10}
Calcium	$C_{\mathrm{Ca}^{++}} \times C_{\mathrm{CrO_4}^=}$	2.3×10^{-2}
Lead	$C_{\mathrm{Pb}^{++}} \times C_{\mathrm{CrO_4}^=}$	1.8×10^{-14}
Silver	$C^2_{\mathrm{Ag}^+} \times C_{\mathrm{CrO_4}^=}$	1.7×10^{-12}

TABLE VII—*Continued*

SOLUBILITY PRODUCTS

Compound	Ions	$K_{\mathrm{s.p.}}$*
Cyanide		
Silver	$C_{\mathrm{Ag}^+} \times C_{[\mathrm{Ag(CN)_2}]^-}$	2.2×10^{-12}
Fluorides		
Barium	$C_{\mathrm{Ba}^{++}} \times C^2_{\mathrm{F}^-}$	1.7×10^{-6}
Calcium	$C_{\mathrm{Ca}^{++}} \times C^2_{\mathrm{F}^-}$	3.5×10^{-11}
Lead	$C_{\mathrm{Pb}^{++}} \times C^2_{\mathrm{F}^-}$	3.5×10^{-8}
Magnesium	$C_{\mathrm{Mg}^{++}} \times C^2_{\mathrm{F}^-}$	7×10^{-9}
Strontium	$C_{\mathrm{Sr}^{++}} \times C^2_{\mathrm{F}^-}$	2.5×10^{-9}
Hydroxides		
Aluminum	$C_{\mathrm{H}^+} \times C_{\mathrm{AlO_2}^-}$	3.7×10^{-15}
Ferric	$C_{\mathrm{Fe}^{+++}} \times C^3_{\mathrm{OH}^-}$	1.1×10^{-36}
Ferrous	$C_{\mathrm{Fe}^{++}} \times C^2_{\mathrm{OH}^-}$	1.6×10^{-14}
Magnesium	$C_{\mathrm{Mg}^{++}} \times C^2_{\mathrm{OH}^-}$	3.4×10^{-11}
Manganous	$C_{\mathrm{Mn}^{++}} \times C^2_{\mathrm{OH}^-}$	4×10^{-14}
Silver	$C_{\mathrm{Ag}^+} \times C_{\mathrm{OH}^-}$	2×10^{-8}
Zinc	$C_{\mathrm{Zn}^{++}} \times C^2_{\mathrm{OH}^-}$	1.0×10^{-18}
Iodates		
Cupric	$C_{\mathrm{Cu}^{++}} \times C^2_{\mathrm{IO_3}^-}$	1.4×10^{-7}
Silver	$C_{\mathrm{Ag}^+} \times C_{\mathrm{IO_3}^-}$	2×10^{-8}
Iodides		
Cuprous	$C_{\mathrm{Cu}^+} \times C_{\mathrm{I}^-}$	5×10^{-12}
Lead	$C_{\mathrm{Pb}^{++}} \times C^2_{\mathrm{I}^-}$	1.4×10^{-8}
Mercurous	$C_{\mathrm{Hg_2}^{++}} \times C^2_{\mathrm{I}^-}$	1.2×10^{-28}
Silver	$C_{\mathrm{Ag}^+} \times C_{\mathrm{I}^-}$	1.5×10^{-16}
Thallous	$C_{\mathrm{Tl}^+} \times C_{\mathrm{I}^-}$	2.8×10^{-8}
Oxalates		
Barium	$C_{\mathrm{Ba}^{++}} \times C_{\mathrm{C_2O_4}^{=}}$	2.2×10^{-7}
Cadmium	$C_{\mathrm{Cd}^{++}} \times C_{\mathrm{C_2O_4}^{=}}$	1.3×10^{-8}
Calcium	$C_{\mathrm{Ca}^{++}} \times C_{\mathrm{C_2O_4}^{=}}$	2.6×10^{-9}
Cupric	$C_{\mathrm{Cu}^{++}} \times C_{\mathrm{C_2O_4}^{=}}$	2.9×10^{-8}
Ferrous	$C_{\mathrm{Fe}^{++}} \times C_{\mathrm{C_2O_4}^{=}}$	2.1×10^{-7}
Lead	$C_{\mathrm{Pb}^{++}} \times C_{\mathrm{C_2O_4}^{=}}$	3.4×10^{-11}
Magnesium	$C_{\mathrm{Mg}^{++}} \times C_{\mathrm{C_2O_4}^{=}}$	8.6×10^{-5}
Silver	$C^2_{\mathrm{Ag}^+} \times C_{\mathrm{C_2O_4}^{=}}$	5×10^{-12}
Strontium	$C_{\mathrm{Sr}^{++}} \times C_{\mathrm{C_2O_4}^{=}}$	5.6×10^{-8}
Zinc	$C_{\mathrm{Zn}^{++}} \times C_{\mathrm{C_2O_4}^{=}}$	1.4×10^{-9}

TABLE VII—*Continued*

SOLUBILITY PRODUCTS

Compound	Ions	$K_{s.p.}$*
Phosphates		
Lead	$C^3_{Pb^{++}} \times C^2_{PO_4^{\equiv}}$	1.5×10^{-32}
Magnesium ammonium	$C_{Mg^{++}} \times C_{NH_4^+} \times C_{PO_4^{\equiv}}$	2.5×10^{-13}
Silver	$C^3_{Ag^+} \times C_{PO_4^{\equiv}}$	1.8×10^{-18}
Sulfates		
Barium	$C_{Ba^{++}} \times C_{SO_4^{=}}$	1.2×10^{-10}
Calcium	$C_{Ca^{++}} \times C_{SO_4^{=}}$	6.1×10^{-5}
Lead	$C_{Pb^{++}} \times C_{SO_4^{=}}$	1.1×10^{-8}
Silver	$C^2_{Ag^+} \times C_{SO_4^{=}}$	7.0×10^{-5}
Strontium	$C_{Sr^{++}} \times C_{SO_4^{=}}$	2.8×10^{-7}
Sulfides		
Arsenic	$C^2_{As^{+++}} \times C^3_{S^{=}}$	4×10^{-29}
Bismuth	$C^2_{Bi^{+++}} \times C^3_{S^{=}}$	1.6×10^{-72} (?)
Cadmium †	$C_{Cd^{++}} \times C_{S^{=}}$	3.8×10^{-28} (av.)
Cobalt	$C_{Co^{++}} \times C_{S^{=}}$	3×10^{-26}
Cupric †	$C_{Cu^{++}} \times C_{S^{=}}$	2.5×10^{-41} (av.)
Cuprous	$C^2_{Cu^+} \times C_{S^{=}}$	2×10^{-47}
Ferrous	$C_{Fe^{++}} \times C_{S^{=}}$	3.7×10^{-19}
Lead †	$C_{Pb^{++}} \times C_{S^{=}}$	3.4×10^{-28}
Manganese (pink?) †	$C_{Mn^{++}} \times C_{S^{=}}$	7.0×10^{-16}
Manganese (green) †		6.2×10^{-22}
Mercuric †	$C_{Hg^{++}} \times C_{S^{=}}$	3×10^{-54}
Mercurous †	$C^2_{Hg^+} \times C_{S^{=}}$	1×10^{-47}
Nickel	$C_{Ni^{++}} \times C_{S^{=}}$	1.4×10^{-24}
Silver †	$C^2_{Ag^+} \times C_{S^{=}}$	1×10^{-50} (av.)
Thallous	$C^2_{Tl^+} \times C_{S^{=}}$	7.0×10^{-23}
Tin	$C_{Sn^{++}} \times C_{S^{=}}$	1×10^{-26}
Zinc (α) †	$C_{Zn^{++}} \times C_{S^{=}}$	6.6×10^{-26} (av.)
Thiocyanates		
Cuprous	$C_{Cu^+} \times C_{CNS^-}$	1.7×10^{-11}
Silver	$C_{Ag^+} \times C_{CNS^-}$	1.2×10^{-12}
Thallous	$C_{Tl^+} \times C_{CNS^-}$	1.4×10^{-4}

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* The temperature in most cases is either 18° or 25°. Ordinarily the $K_{s.p.}$ may be considered as being independent of the temperature over the range of 15° to 35°.

† Kolthoff, *J. Phys. Chem.*, **35**, 2711 (1931).

Solubility Product and Speed of Equilibrium Attainment. Although the solubility-product equation defines a state of equilibrium, it makes no mention of the speed at which equilibrium is reached. It simply states that precipitation cannot take place until the value of the $K_{s.p.}$ is exceeded by the ion concentration product, but it is no guarantee that precipitation will occur *at once* when the $K_{s.p.}$ is exceeded. As a matter of fact, small amounts (i.e., up to about 5 mg.) of many slightly soluble salts (e.g., CuS, SnS, $BaSO_4$, $MgNH_4PO_4$, etc.) require from 14 to 48 hours before precipitation is complete and equilibrium is attained.[3] For small amounts of these salts a certain time must elapse before a precipitate appears, and then a further, and often much longer, period must elapse before precipitation is complete. Vigorous shaking or stirring or the use of a centrifuge will often greatly speed up the precipitation.

Total Precipitation Impossible. It must be remembered that **total** precipitation of a compound is impossible, that is, no compound is **totally** insoluble. No matter how greatly the concentration of one ion is increased, the concentration of the other cannot be reduced to zero. This follows from the solubility-product law and may be illustrated graphically, using the respective ionic concentrations as coordinates. With salts of the BA type the graph will be an equilateral hyperbola (see Fig. 6). Similar curves are obtained for salts of the BA_2, B_2A, BA_3, B_3A, B_2A_3, etc., types. The hyperbola never intersects the coordinate axes but approaches them and finally becomes sensibly parallel to them. The graph also emphasizes the fact that, after a certain point, further excess of the precipitating reagent (i.e., ion) accomplishes very little. In other words, only a **moderate** excess of a common ion need be added in precipitation reactions. As a matter of fact, a large excess of reagent is frequently to be avoided, as secondary reactions would take place. For example, in precipitating the Silver Group with hydrochloric acid, only a small excess of the

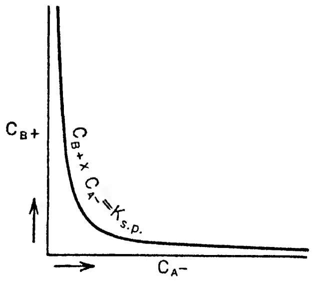

Fig. 6

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[3] Fales, "Inorganic Quantitative Analysis," p. 170, the Century Co., New York, 1925.

acid is added, as a high chloride-ion concentration would dissolve the AgCl, $PbCl_2$, and Hg_2Cl_2, owing to the formation of complex anions of the type $[AgCl_3]^{=}$, $[PbCl_4]^{=}$, and $[Hg_2Cl_4]^{=}$. Again, with aluminum and chromic hydroxides, a large excess of ammonium hydroxide would redissolve some of the precipitate, owing to the formation of soluble NH_4AlO_2 and a soluble red complex, respectively.

Fractional Precipitation. Fractional precipitation is discussed in Chapter XV in connection with problems involving applications of the solubility-product principle.

Co-Precipitation.[4] It has been known for a long time that crystalline precipitates separating from a solution are not, as a rule, quite pure but usually contain imperfections of mother liquor with foreign constituents. A vast number of empirical facts pertaining to the presence of various impurities in crystalline precipitates may be found in the analytical literature. Unfortunately, these data are of not much use in the interpretation of the so-called "co-precipitation" or "carrying down," mainly for the reason of poor description of experimental conditions, . . . which are of primary influence as regards the kind and amount of co-precipitation. Moreover, it has been a general custom in analytical chemistry to use the words, co-precipitation, carrying down [dragging down], occlusion, inclusion and adsorption as collective names, meaning nothing else but the establishment of the fact that impurities are carried down with or in a precipitate. In a systematic treatment of the problem, it should be emphasized, however, that *three different phenomena mainly account for the presence of impurities in the precipitate* and in a study of the problem, it is necessary first to find out the kind of co-precipitation with which we are dealing.

Kolthoff distinguishes four cases:

I. *The formation of mixed crystals.* In this case the impurities are *incorporated* in the *crystal lattice* and they do not change the regular structure of the latter. The amount of mixed crystal formation depends (as in case III) upon adsorption phenomena during the growth of the precipitate.

II. *Occlusion* (Real Co-precipitation). In this case the impurities are not incorporated in the crystal lattice, but *they are adsorbed during the growth of the crystals* and give rise to the formation of *imperfections* in the crystal. ("Hohlräume or Lockerstellen" [Smekal]; or centra of activity—[H. S. Taylor].) Here adsorption phenomena during the growth of the crystals are mainly responsible for the amount of occlusion. . . .

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[4] Kolthoff, *J. Phys. Chem.*, **36**, 860 (1932).

III. *Surface adsorption by the precipitate after it has been formed or separated.* This kind of co-precipitation is only of practical importance when the precipitate has a large surface, i.e., when it behaves like a flocculated colloid. If the precipitate has a definitely micro-crystalline character (as observed under the microscope) the amount of co-precipitation caused by surface adsorption is, as a rule, of no practical significance. Confusion is caused in the analytical literature by the fact that certain phenomena have been attributed to co-precipitation (an expression often used to indicate that a precipitate is not quite pure), but which have nothing to do with it. This may be illustrated by two examples. In most text books of analytical chemistry, it is mentioned that magnesium is co-precipitated with calcium oxalate. Although there is actually a slight co-precipitation of this element, the presence of magnesium in calcium oxalate, if the latter is precipitated from solutions containing much magnesium salt, is mainly due to the slight solubility of magnesium oxalate. If relatively much magnesium is present and an excess of oxalate is added, the solution becomes supersaturated with respect to magnesium oxalate. First of all, calcium oxalate precipitates and then on standing magnesium oxalate crystallizes out slowly. Therefore, we are not dealing here with a case of co-precipitation, but of *post-precipitation,* the crystals of calcium oxalate being not at all or only slightly contaminated by magnesium. The magnesium oxalate crystallizes out as a separate phase. . . . Another example of post-precipitation is the so-called "co-precipitation of zinc with copper sulfide." . . .

IV. A case which rarely occurs is that co-precipitation actually has to be attributed to the formation of a definite chemical compound. The so-called co-precipitation of alkali oxalate with lanthanum oxalate is caused by the formation of a double oxalate as has been shown by I. M. Kolthoff and R. Elmquist.[5] From experiments of Z. Karaoglanov and R. Sargotschev,[6] it appears that co-precipitation of lead bromide and lead chloride with lead oxalate is due to the formation of a double salt $(PbX)_2Ox$. However, the formation of such definite chemical compounds is very seldom encountered in analytical work, although it should not be overlooked as a possible interpretation of the presence of much "impurity" in the precipitate.

Kolthoff has made an attempt to formulate a general theory of co-precipitation, especially of the kind referred to as occlusion. "The hope is expressed that such a theory will not only contribute to the understanding of the formation of impurities in precipitates formed under analytical conditions and thereby the improvement

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[5] Kolthoff and Elmquist, *J. Am. Chem. Soc.*, **53**, 1232 (1931).

[6] Karaoglanov and Sargotschev, *Z. anorg. allgem. Chem.*, **199**, 7 (1931).

of the exact precipitation procedures, but will also have a wider bearing on the problems of mineralogical formations and the properties of slightly soluble micro-crystalline precipitates."

The outstanding facts about the phenomenon of co-precipitation, so far as our present-day knowledge goes, are these:

1. The action is specific.
2. Co-precipitation occurs at the time of the formation of the precipitate. Or, according to Kolthoff, "in the case of real co-precipitation, the adsorption of foreign ions during the growth of the particles is of primary importance."
3. The amount of co-precipitation is a function of the concentration of the salt carried down.
4. Up to a certain limit, co-precipitation with a slightly soluble compound **increases** with crystal size.

For a more detailed study of the theory of co-precipitation the student is referred to Kolthoff's paper in the *Journal of Physical Chemistry,* **36,** 860 (1932). See also, Fales' "Inorganic Quantitative Analysis," page 175.

The Le Chatelier-Braun Principle. The Le Chatelier-Braun principle is one of the most useful generalizations in chemistry, as it is applicable to all systems at equilibrium, regardless of whether they are homogeneous or heterogeneous. It may be stated thus: **If to a system at equilibrium some force or stress is applied, the system will shift in a way which tends to relieve or to diminish the effect of the force or stress.** This theorem really follows from the second law of thermodynamics which may be stated in a general form as follows: All systems tend to approach a state of equilibrium. The term "force" or "stress" refers to temperature, pressure, and concentration, which are the chief factors conditioning the equilibrium of a system. By means of the Le Chatelier-Braun theorem, it is possible to predict *qualitatively* the direction in which a change in a system may be expected. The solubility-product principle is an application of this theorem. All ionic double decomposition equilibria shift in the direction toward which there is a decrease in ion concentration. We may summarize the various ways in which the concentration of any given ion can be decreased:

1. By the formation of a very slightly soluble compound.
2. By means of the common-ion effect.

3. By the formation of a weakly ionized compound, e.g., hydrolysis, formation of an amphoteric substance, displacement of a weak acid from its salts by a stronger acid, etc.
4. By the formation of a complex ion.
5. By a change in the valence of the ion, i.e., oxidation or reduction.

Other examples of the application of the Le Chatelier-Braun principle are: the melting of ice under pressure, the influence of temperature on solubility, the influence of pressure on the solubility of gases, and the influence of pressure on the synthesis of ammonia from nitrogen and hydrogen in the presence of a catalyst.

In the next seven chapters we will discuss some of the more common types of equilibria, both homogeneous and heterogeneous, and will give illustrative problems with particular reference to their applications in analytical chemistry.

CHAPTER XIII

UNITS OF WEIGHT, VOLUME, AND CONCENTRATION USED IN EQUILIBRIA CALCULATIONS

Calculation of Gram-Atom, Gram-Mol, and Gram-Ion Quantities. In all stoichiometric calculations based upon the **law of combining weights,** the **gram** is taken as the unit of mass or weight. Problems involving an application of the **law of chemical equilibrium** employ different units of mass or weight designated by the terms **gram-atom, gram-mol,** and **gram-ion.** When an element is in the atomic state, its unit mass is called a gram-atom; for compounds or uncharged radicals, the unit mass is the gram-mol; and when an atom or radical is ionized, the unit mass is called a gram-ion. Hence, the use of the terms gram-atom, gram-mol, and gram-ion is simply a convenient way to express the unit mass when applied to matter in the atomic, molecular, or ionic state. It is important that the student thoroughly understand these terms and use them correctly.

A **gram-atom,** also called a gram-atomic weight, is the atomic weight of an element expressed in grams. Thus, a gram-atom of hydrogen is 1.008 g. of hydrogen; a gram-atom of oxygen is 16.000 g. of oxygen; a gram-atom of lead is 207.22 g. of lead; etc.

A **gram-mol,** also called a gram-molecular weight or simply a mol, is the molecular weight of a substance expressed in grams. For example, a gram-mol of hydrogen gas is 2.016 g. of hydrogen; a gram-mol of oxygen gas is 32.000 g. of oxygen; a gram-mol of lead chloride is 242.677 g. of lead chloride; a gram-mol of ammonia is 17.032 g. of ammonia; etc.

A **gram-ion** is the atomic or molecular weight of an ion expressed in grams. If the ion is a simple one, consisting only of a charged atom, the atomic weight in grams is 1 gram-ion. Thus, a gram-ion of H^+ ions is 1.008 g. of H^+ ions; a gram-ion of Pb^{++} ions is 207.22 g. of Pb^{++} ions; etc. If the ion consists of a charged group of atoms, for example the ammonium ion, NH_4^+, the carbonate ion, $CO_3^{=}$, the phosphate ion, $PO_4^{\equiv}$, then a gram-ion is the molecular weight of the charged radical expressed in grams. When 1 gram mol of NH_4Cl is dissolved in water, and if the dilution is such that complete ionization may be assumed, then there are present in the solution 1 gram-ion of NH_4^+ ions and 1 gram-ion of Cl^- ions. Similarly, 1 gram-mol of $(NH_4)_3PO_4$ in dilute aqueous solution yields 3 gram-ions of NH_4^+ ions and 1 gram-ion of $PO_4^{\equiv}$ ions.

Case 1. Given the weight in grams of a compound. Calculate the gram-mol quantity.

Example. Calculate the gram-mol quantity represented by 18.233 g. of HCl.

$$\frac{\text{Weight in grams}}{\text{Molecular weight}} = \text{Gram-mols}$$

Hence,

$$\frac{18.233}{36.465} = 0.5 \text{ gram-mol}$$

Case 2. Given the weight in grams of a compound. Calculate the gram-atom quantities of each element.

Example. Calculate the gram-atom quantities of hydrogen and of chlorine in 18.233 g. of HCl.

1. Calculate the gram-mol quantity.

$$\frac{\text{Weight in grams}}{\text{Molecular weight}} = \frac{18.233}{36.465} = 0.5 \text{ gram-mol}$$

2. Write the equation representing the number of gram-atoms of each element contained in 1 gram-mol of the compound.

$$HCl \rightleftharpoons H^+ + Cl^-$$

Hence, 1 gram-mol of HCl contains 1 gram-atom of H and 1 gram-atom of Cl. Therefore, 0.5 gram-mol of HCl contains 0.5 gram-atom of H and 0.5 gram-atom of Cl.

Case 3. Given the weight in grams of an electrolyte. Calculate the gram-ion quantities of each ion which can be obtained when the compound is completely ionized.

Example 1. Calculate the gram-ion quantities of H^+ ions and of Cl^- ions which can be obtained from 18.233 g. of HCl.

1. Calculate the gram-mol quantity. In the preceding example, this was found to be 0.5 gram-mol.

2. Write the equation representing the ionization of 1 gram-mol of HCl.

$$HCl \rightleftharpoons H^+ + Cl^-$$

Since 1 gram-mol of HCl yields, upon complete ionization, 1 gram-ion of H^+ ions and 1 gram-ion of Cl^- ions, it follows that 0.5 gram-mol of HCl will yield 0.5 gram-ion of H^+ ions and 0.5 gram-ion of Cl^- ions.

Example 2. Calculate the gram-ion quantities of each ion which can be obtained from 1 gram-mol of $PbCl_2$.

Lead chloride ionizes according to the following equation:

$$PbCl_2 \rightleftharpoons Pb^{++} + 2Cl^-$$

Therefore, 1 gram-mol of $PbCl_2$ will yield 1 gram-ion of Pb^{++} ions and 2 gram-ions of Cl^- ions.

Example 3. Calculate the gram-ion quantities of each ion which can be obtained from 1 gram-mol of K_2CrO_4.

Potassium chromate ionizes according to the following equation:

$$K_2CrO_4 \rightleftharpoons 2K^+ + CrO_4^{=}$$

Hence, 1 gram-mol of K_2CrO_4 will yield 2 gram-ions of K^+ ions and 1 gram-ion of $CrO_4^{=}$ ions.

Case 4. Given the quantity of a substance in terms of gram-mols. Calculate its weight in grams. This is the reverse of Case 1.

Example. How many grams of silver chloride are contained in 0.1 gram-mol of AgCl?

$$\text{Gram-mols} \times \text{Molecular weight} = \text{Weight in grams}$$
$$0.1 \times 143.337 = 14.3337 \text{ g. of AgCl}$$

Case 5. Given the quantity of a compound in terms of gram-mols. Calculate the weight in grams of each atom or ion.

Example 1. How many grams of Fe and of S are contained in 0.1 gram-mol of FeS?

Ferrous sulfide is formed according to the following equation:

$$Fe + S \rightarrow FeS$$

Hence, 1 gram-atom of Fe and 1 gram-atom of S are required to form 1 gram-mol of FeS. Therefore, 0.1 gram-atom of Fe and 0.1 gram-atom of S are contained in 0.1 gram-mol of FeS.

$$\begin{aligned} \text{Atomic weight of Fe} &= 55.84 \\ \text{Atomic weight of S} &= 32.06 \\ \text{Gram-atom} \times \text{Atomic weight} &= \text{Weight in grams} \\ 0.1 \times 55.84 &= 5.584 \text{ g. of Fe} \\ 0.1 \times 32.06 &= 3.206 \text{ g. of S} \end{aligned}$$

Example 2. Calculate the grams of Ag^+ ions and $PO_4^{\equiv}$ ions formed upon complete ionization of 0.01 gram-mol of Ag_3PO_4.

Silver phosphate ionizes as follows:

$$Ag_3PO_4 \rightleftharpoons 3Ag^+ + PO_4^{\equiv}$$

Therefore, for each mol of Ag_3PO_4 there are formed 3 gram-ions of Ag^+ ions and 1 gram-ion of $PO_4^{\equiv}$ ions.

$$\begin{aligned} \text{Atomic weight of } Ag^+ &= 107.88 \\ \text{Molecular weight of } PO_4^{\equiv} &= 95.02 \\ 0.03 \times 107.88 &= 3.2364 \text{ g. of } Ag^+ \text{ ion} \\ 0.01 \times 95.02 &= 0.9502 \text{ g. of } PO_4^{\equiv} \text{ ion} \end{aligned}$$

In the above problems dealing with solutions of electrolytes it was assumed that ionization is complete. This assumption may be made for dilute solutions of strong electrolytes and for extremely dilute solutions of weak electrolytes. Otherwise, it is necessary to know the degree of ionization, i.e., percentage of ionization, in order to calculate the weight of ions and of non-ionized molecules obtained upon dissolving a given amount of electrolyte. The weight of the ions and of the non-ionized molecules may be expressed either in gram-ion and gram-mol quantities, respectively, or in gram quantities.

Case 6. Given the quantity of an electrolyte present in solution and its percentage ionization. Calculate the amounts of each ion and of non-ionized solute.

Example 1. Calculate the gram-ion amounts of Na^+ ion and $C_2H_3O_2^-$ ion and of non-ionized $NaC_2H_3O_2$ in a liter of 0.1 *M* solution of sodium acetate which is 80 per cent ionized.

Sodium acetate ionizes as follows:

$NaC_2H_3O_2$	$\rightleftharpoons$	Na^+	$+$	$C_2H_3O_2$
1 gram-mol		1 gram-ion		1 gram-ion
0.1 gram-mol		0.1 gram-ion		0.1 gram-ion
Fraction non-ionized		Fraction ionized		
0.20		0.80		

Hence, the solution contains:

$$\begin{aligned} 0.1 \times 0.80 &= 0.080 \text{ gram-ion of } Na^+ \text{ ion} \\ 0.1 \times 0.80 &= 0.080 \text{ gram-ion of } C_2H_3O_2^- \text{ ion} \\ 0.1 \times 0.20 &= 0.020 \text{ gram-mol of non-ionized } NaC_2H_3O_2 \end{aligned}$$

Example 2. Express the gram-ion and gram-mol quantities in example 1 in terms of gram weight.

$$\begin{aligned} \text{Atomic weight of } Na^+ &= 23.0 \\ \text{Molecular weight of } C_2H_3O_2^- &= 59.0 \end{aligned}$$

Molecular weight of $NaC_2H_3O_2$ = 82.0
0.080 × 23.0 = 1.84 g. of Na^+ ions
0.080 × 59.0 = 4.72 g. of $C_2H_3O_2^-$ ions
0.020 × 82.0 = 1.64 g. of non-ionized $NaC_2H_3O_2$

8.20 g. of total solute, which is the amount required to prepare a liter of 0.1 *M* solution of sodium acetate.

PROBLEMS

1. How many gram-atoms are represented by each of the following:
   (*a*) 20.72 g. of lead (Pb)?
   (*b*) 0.6357 g. of copper (Cu)?
   (*c*) 26.97 g. of aluminum (Al)?

2. Calculate the gram-atoms represented by:
   (*a*) 3.9×10^{-5} g. of potassium (K).
   (*b*) 2.3×10^{3} g. of sodium (Na).
   (*c*) 6.9×10^{-8} g. of lithium (Li).

3. How many gram-atoms of each element are contained in 53.50 g. of NH_4Cl? In 260.02 g. of $Bi(OH)_3$? In 310.28 g. of $Ca_3(PO_4)_2$?

4. Convert the following gram-atom quantities into grams of the respective metals:
   (*a*) 3.521 gram-atoms of iron (Fe).
   (*b*) 0.789 gram-atom of chromium (Cr).
   (*c*) 0.066 gram-atom of zinc (Zn).

5. How many gram-atoms of each element are contained in 1 gram-mol of $BaSO_4$? In 1 gram-mol of $CaCO_3$? In 1 gram-mol of $MgNH_4PO_4$?

6. How many grams in 1 gram-mol of each of the following compounds:
   (*a*) Hg_2Cl_2?
   (*b*) As_2S_5?
   (*c*) $Al(OH)_3$?

7. Convert the following gram quantities into gram-mols:
   (*a*) 15.24 g. of K_2CrO_4.
   (*b*) 0.581 g. of N_2.
   (*c*) 0.034 g. of H_2S.

8. Express the following gram amounts in terms of gram-mols:
   (*a*) 4.4×10^{-10} g. of CO_2.
   (*b*) 3.81×10^{-6} g. of Cu_2I_2.
   (*c*) 4.19×10^{-3} g. of Ag_3PO_4.

9. Calculate to gram weight the following:
   (*a*) 8.35×10^{-4} gram-mol of HCl.
   (*b*) 2.91×10^{-7} gram-mol of H_2SO_4.
   (*c*) 5.46×10^{-12} gram-mol of H_3PO_4.

10. Calculate the gram weight of each element in the molar quantities of the following substances:

(a) 0.5 gram-mol of Cu_2Br_2.
(b) 2.7×10^3 gram-mols of $CuBr_2$.
(c) 6.4×10^{-3} gram-mol of $SnCl_4$.

11. Express the following gram quantities in terms of the gram-ion:

(a) 112.4 g. of Cd^{++} ions.
(b) 54.9 g. of Mn^{++} ions.
(c) 58.7 g. of Ni^{++} ions.

12. How many gram-ions are present in each of the following:

(a) 35.5 g. of Cl^- ions.
(b) 60.0 g. of $CO_3^=$ ions.
(c) 95.0 g. of $PO_4^{\equiv}$ ions.

13. Convert the following milligram weights into millimols:

(a) 2.7×10^5 mg. of O_2.
(b) 6.5×10^8 mg. of Cl_2.
(c) 1.2×10^{12} mg. of H_2.

14. How many milligrams of each compound are represented by the following quantities:

(a) 3.4×10^{-9} millimol of CoS?
(b) 7.2×10^{-11} millimol of BaC_2O_4?
(c) 2.8×10^{-15} millimol of $SrSO_4$?

15. How many milligrams of each of the following substances are required to make 1 gram-mol, respectively:

(a) $CuSO_4 \cdot 5H_2O$?	*Ans.* (a) 2.50×10^5 mg.
(b) $MgCO_3 \cdot (NH_4)_2CO_3 \cdot 4H_2O$?	(b) 2.52×10^5 mg.
(c) $K_4Fe(CN)_6 \cdot 3H_2O$?	(c) 4.22×10^5 mg.

16. A 0.1 *M* solution of hydrochloric acid is 93.0 per cent ionized at 18° C. Calculate the gram-ion quantity of H^+ ion and Cl^- ion and the gram-mol amount of undissociated HCl per liter of the solution

Ans. 0.092, 0.008.

17. Calculate the gram-ion quantities of H^+ ion and $C_2H_3O_2^-$ ion in a liter of 0.1 *M* $HC_2H_3O_2$, which is 1.34 per cent ionized at 18° C.

Ans. 1.34×10^{-3}.

18. (a) What is the weight of un-ionized NH_4OH in a 0.1 *M* NH_4OH solution which is 1.31 per cent ionized at 18° C.? (b) What are the gram-ion amounts of NH_4^+ ion and OH^- ion?

Ans. (a) 3.45 g. per l.
(b) 1.31×10^{-3}.

19. A 0.01 *M* solution of $MgSO_4$ is 59.6 per cent ionized at 18° C. Calculate the gram-ion quantity of Mg^{++} ion in 1 liter of the solution.

Ans. 5.96×10^{-3}.

20. Calculate the gram-ion quantities of OH^- ion in 1 liter of NH_4OH solutions of the following strengths:

(*a*) 1 *M* (0.4 per cent ionized at 18° C.).

Ans. (*a*) 4.0×10^{-3}.

(*b*) 0.01 *M* (4.07 per cent ionized at 18° C.).

Ans. (*b*) 4.1×10^{-4}.

(*c*) 0.001 *M* (11.7 per cent ionized at 18° C.).

Ans. (*c*) 1.17×10^{-4}.

21. What are the gram-ion quantities of K^+ ion in 1 liter of K_2SO_4 solutions of the following concentrations:

(*a*) 0.1 *M* (67.3 per cent ionized at 18° C.)?

Ans. (*a*) 0.135.

(*b*) 0.01 *M* (83.2 per cent ionized at 18° C.)?

Ans. (*b*) 1.66×10^{-2}.

(*c*) 0.001 *M* (93.7 per cent ionized at 18° C.)?

Ans. (*c*) 1.87×10^{-3}.

22. Hydrofluoric acid is 8.5 per cent ionized in 0.1 *M* solution. What is the gram-ion quantity of H^+ ion in 1 liter?

Ans. 8.5×10^{-3}.

23. Sodium acetate is 89.4 per cent ionized in 0.01 *M* solution at 18° C. What are the gram-ion quantities of Na^+ ion and $C_2H_3O_2^-$ ion in 1 liter?

Ans. 8.94×10^{-3}.

24. Compare the gram-ion quantities of H^+ ion in 1 liter of each of the following acids:

(*a*) 0.1 *M* HNO_3 (92 per cent ionized at 18° C.)

Ans. (*a*) 9.2×10^{-2}.

(*b*) 0.1 *M* HNO_2 (8 per cent ionized at 18° C.).

Ans. (*b*) 8.0×10^{-3}.

(*c*) 0.1 *M* HCN (0.01 per cent ionized at 18° C.).

Ans. (*c*) 1.0×10^{-5}.

25. Solutions, 0.1 *M*, of NH_4OH, $Ba(OH)_2$, and NaOH are 1.3, 77, and 91 per cent ionized, respectively, at 18° C. Compare their gram-ion OH^- ion strengths.

Ans. (*a*) 1.3×10^{-3}.
(*b*) 0.154.
(*c*) 9.1×10^{-2}.

Calculation of Molar and Gram-Ion Concentrations. It was stated on page 106 that problems involving an application of the **law of chemical equilibrium** employ the **gram-mol** and **gram-ion** unit of weight instead of the **gram** unit used in all stoichiometric calculations based upon the **law of combining weights.** In a study of equilibrium relationships in solutions it is necessary to state the

concentration of the solute molecules and ions in terms of gram-mol and gram-ion quantities, respectively, per given volume of solution involved in the equilibrium.

The molar solution and molar concentration are used in the equilibrium problems which follow. A **molar solution** is one which contains a gram-molecular weight of solute per liter of solution. This solution must not be confused with a **molal solution** which is one containing a gram-molecular weight of solute per **1000 grams of solvent.** Note that the term "molal" refers to a weight concentration, whereas the term "molar" refers to a volume concentration. When the density of the solution is known, a molal solution may be converted into a molar solution, and *vice versa.*

Unit of Volume. For the sake of uniformity, scientific laboratories have adopted, as the unit of volume, the **liter,** as established by the International Commission of Weights and Measures[1] in 1880. Originally the Commission worded the definition of the liter as follows: "The liter is the volume of a kilogram of pure water at its maximum density." Later, in 1901, the Commission amplified the definition to read: "The liter is the volume occupied by the mass of one kilogram of pure water at its maximum density and under normal atmospheric pressure." The definition used by the United States National Bureau of Standards[2] is: "The liter is the volume occupied by a quantity of pure water at 4° C., having a mass of one kilogram." These definitions are all substantially equivalent.

Since the liter is derived with the aid of the unit of mass (the kilogram) rather than with the unit of length (the meter), its subdivisions are, strictly speaking, called milliliters instead of cubic centimeters. However, the difference between 1 liter and 1000 cc. is so small that it has no practical significance in analytical chemistry. Actually 1 liter equals 1000.028 cc. In the problems which follow we will use the term "milliliter" instead of the cubic centimeter. The abbreviation for the milliliter is ml., often written mil.

Case 7. Given the quantity of a substance contained in a certain volume of solution. Calculate the molar concentration of the solution.

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[1] Procès-Verbaux, Comité International Poids et Mesures, 30 (1880).

[2] Bureau of Standards, Reprint 92. Osborne and Veazey, "The Testing of Glass Volumetric Apparatus," p. 565. Washington, D. C. (1908).

Example 1. What is the molar (M) concentration of an ammonium chloride solution which contains 16.049 g. of NH_4Cl per 100 ml. of solution?

$$\begin{aligned} 16.049 \times 10 &= 160.49 \text{ g. of } NH_4Cl \text{ per liter} \\ 1 \text{ mol of } NH_4Cl &= 53.496 \text{ g.} \\ \therefore \quad 160.49 \div 53.496 &= 3 \text{ mols} \end{aligned}$$

Hence, the solution of NH_4Cl is 3 M.

Example 2. Calculate the molarity of an ammonium hydroxide solution which contains 28.33 per cent of NH_3 (by weight) and has a specific gravity of 0.900.

$$\begin{aligned} 1000 \times 0.2833 \times 0.900 &= 255 \text{ g. of } NH_3 \text{ in 1 liter} \\ 1 \text{ mol of } NH_3 &= 17 \text{ g.} \\ \therefore \quad 255 \div 17 &= 15 \text{ mols } NH_3. \end{aligned}$$

Hence, the solution of $NH_4OH(NH_3 + H_2O)$ is 15 M.

Case 8. Given the quantity of an electrolyte contained in a certain volume of solution: Calculate the gram-ion concentrations of each kind of ion present in the solution and the gram-mol concentration of the non-ionized solute.

Example 1. Calculate the gram-ion concentrations of NH_4^+ ions and OH^- ions and the gram-mol concentration of non-ionized NH_4OH in a liter of 1 M NH_4OH solution which is 0.4 per cent ionized.

$$\begin{array}{lccccl} & NH_4OH & \rightleftharpoons & NH_4^+ & + & OH^- \\ \text{(Fraction non-ionized)} & 0.996 & & 0.004 & & 0.004 \quad \text{(Fraction ionized)} \end{array}$$

$\therefore$ NH_4^+ concentration is 0.004 gram-ion per liter
OH^- concentration is 0.004 gram-ion per liter
NH_4OH (non-ionized) conc. is 0.996 gram-mol per liter

Example 2. What are the Ba^{++} ion and the Cl^- ion concentrations in a solution made by dissolving 2.083 g. of $BaCl_2$ in water and diluting to 100 ml.? Assume 100 per cent ionization.

$$\begin{aligned} 2.083 \times 10 &= 20.83 \text{ g. } BaCl_2 \text{ per liter} \\ \text{Mol. wt. } BaCl_2 &= 208.3 \\ \therefore \quad 20.83 \div 208.3 &= 0.1\ M \ BaCl_2 \text{ solution} \end{aligned}$$

$$\begin{array}{ccccc} BaCl_2 \rightleftharpoons & Ba^{++} & + & 2Cl^- \\ 0.1 \text{ mol} & 0.1 \text{ gram-ion} & & 0.2 \text{ gram-ion} \end{array}$$

Hence, the solution contains 0.1 gram-ion of Ba^{++} ions and 0.2 gram-ion of Cl^- ions per liter.

Case 9. Given the molarity of an electrolyte and its degree of ionization. Calculate the gram-ion concentration of its ions and the molar concentration of the non-ionized solute.

Example. 1. A 0.01 *M* solution of acetic acid is 4.2 per cent ionized at 25° C. Calculate the gram-ion concentrations of the H^+ ions and $C_2H_3O_2{}^-$ ions and the molar concentration of non-ionized $HC_2H_3O_2$.

Acetic acid ionizes according to the following reaction:

$$HC_2H_3O_2 \rightleftharpoons H^+ + C_2H_3O_2{}^-$$

When the 0.01 *M* $HC_2H_3O_2$ reaches equilibrium at 25° C., 4.2 per cent will be ionized. Hence $0.01 \times 0.042 = 0.00042$ mol per liter is completely ionized, while $0.01 - 0.00042 = 0.00958$ mol per liter remains un-ionized. Each mol of $HC_2H_3O_2$ on complete ionization yields 1 gram-ion of H^+ ions and 1 gram-ion of $C_2H_3O_2{}^-$ ions. Hence 0.00042 mol of $HC_2H_3O_2$ per liter will yield 0.00042 gram-ion of H^+ ions and 0.00042 gram-ion of $C_2H_3O_2{}^-$ ions per liter.

Example 2. A 0.01 *M* solution of potassium sulfate is 83.2 per cent ionized at 18° C. Calculate the gram-ion concentrations of K^+ ions and $SO_4{}^=$ ions and the molar concentration of non-ionized K_2SO_4.

Potassium sulfate ionizes as follows:

$$K_2SO_4 \rightleftharpoons 2K^+ + SO_4{}^=$$

When the 0.01 *M* K_2SO_4 reaches equilibrium at 18° C., 83.2 per cent will be ionized. Hence $0.01 \times 0.832 = 0.00832$ mol per liter is completely ionized, while $0.01 - 0.00832 = 0.00168$ mol per liter remains un-ionized. Each mol of K_2SO_4 on complete ionization yields 2 gram-ions of K^+ ions and 1 gram-ion of $SO_4{}^=$ ions. Hence 0.00832 mol of K_2SO_4 per liter will yield $2 \times 0.00832 = 0.01664$ gram-ion of K^+ ions and 0.00832 gram-ion of $SO_4{}^=$ ions per liter.

The different types of electrolytes may be represented by the following formulas: B^+A^-, $B_2{}^+A^=$, $B^{++}A_2{}^-$, $B^{+++}A_3{}^-$, $B_3{}^+A^{\equiv}$, $B_2{}^{+++}A_3{}^=$, $B_3{}^{++}A_2{}^{\equiv}$, etc.

In computing the gram-ion concentrations:

1. Calculate the gram-mol quantity of substance present in 1 liter of solution.

2. Write the equation representing the ionization of the substance.

E.g.,

$$\begin{array}{ccccc} B^+A^+ & \rightleftharpoons & B^+ & + & A^- \\ \text{1 mol} & & \text{1 gram-ion} & & \text{1 gram-ion} \end{array}$$

$$\begin{array}{ccccc} B_2{}^+A^= & \rightleftharpoons & 2B^+ & + & A^= \\ \text{1 mol} & & \text{2 gram-ions} & & \text{1 gram-ion} \end{array}$$

$$\begin{array}{ccccc} B^{+++}A_3{}^- & \rightleftharpoons & B^{+++} & + & 3A^- \\ \text{1 mol} & & \text{1 gram-ion} & & \text{3 gram-ions} \end{array}$$

$$\begin{array}{ccccc} B_2{}^{+++}A_3{}^= & \rightleftharpoons & 2B^{+++} & + & 3A^= \\ \text{1 mol} & & \text{2 gram-ions} & & \text{3 gram-ions} \end{array}$$

3. If ionization is 100 per cent, then the gram-ion concentrations may be obtained directly from 2. If ionization is not complete, then multiply the gram-ion values in 2 by the fraction of the electrolyte which is ionized.

4. When the molarity is 1, the concentration of non-ionized solute is obtained by subtracting the fraction ionized from the total molar concentration. Thus in Case 8, Example 1, the concentration of non-ionized NH_4OH is $1 - 0.004 = 0.996$ mol per liter. When the molarity is not 1, then the concentration of the non-ionized solute is obtained by multiplying the non-ionized fraction by the total molar concentration.

PROBLEMS

1. How many grams of each of the following acids are required to make 1 liter of molar solutions: HCl, H_2SO_4, and H_3PO_4?

2. Calculate the grams of each of the following bases that must be taken to make 1 liter of 0.1 *M* solutions: NaOH, KOH, and $Ba(OH)_2$.

3. A liter of each of the following solutions is known to contain the amount of the salt indicated. What are their molar strengths?

(*a*) 16.99 g. of $AgNO_3$.
(*b*) 160.5 g. of NH_4Cl.
(*c*) 41.65 g. of $BaCl_2$.

4. From the following gram concentrations per liter, calculate the molar strengths:

(*a*) 68.14 g. of $(NH_4)_2S$.
(*b*) 342.3 g. of $(NH_4)_2CO_3 \cdot H_2O$.
(*c*) 358.2 g. of $Na_2HPO_4 \cdot 12H_2O$.

5. How many grams of each of the following salts are required to prepare 0.1 *M* solutions of each: K_2CrO_4, $NaC_2H_3O_2$, and $K_4Fe(CN)_6$?

6. Calculate the gram-ion concentrations of the respective ions in the following solutions, assuming complete ionization:

(*a*) Solution containing 5.845 g. of NaCl per liter.
(*b*) Solution containing 10.42 g. of $Pb(NO_3)_2$ per liter.
(*c*) Solution containing 132.1 g. of $(NH_4)_2SO_4$ per liter.

7. Calculate the gram-ion concentrations of the respective ions in the following 0.1 *M* solutions: $AgNO_3$, $CaCl_2$, and Na_3PO_4. (Assume 100 per cent ionization.)

8. (*a*) A 0.1 *M* solution of acetic acid is 1.34 per cent ionized at 18° C. What are the H^+ ion and $C_2H_3O_2^-$ ion concentrations? (*b*) What is the gram-mol concentration of un-ionized acetic acid?

9. Calculate the OH^- ion concentration in 0.1 *M* NH_4OH solution which is 1.31 per cent ionized at 18° C.

10. What is the H^+ ion concentration of each of the following hydrochloric acid solutions:

(*a*) 1 *M* HCl, 80 per cent ionized at 18° C.?
(*b*) 0.1 *M* HCl, 92 per cent ionized at 18° C.?
(*c*) 0.01 *M* HCl, 97 per cent ionized at 18° C.?

11. Calculate the molar concentration of each of the following saturated solutions:

(*a*) 0.021 g. of AgCl per liter at 100° C.
(*b*) 0.0023 g. of $BaSO_4$ per liter at 18° C.
(*c*) 0.0044 g. of $BaCrO_4$ per liter at 28° C.

12. What is the gram-metallic-ion concentration of each solution in problem 11? (Assume 100 per cent ionization.)

13. Suppose that "test solutions" contain 10 mg. of the "test ion" per milliliter of solution. Calculate the gram-ion concentration of each of the following ions in the "test solutions," assuming complete ionization: Ag^+, Cd^{++}, Bi^{+++}, Cl^-, and $SO_4^=$.

14. A molar solution of $NaC_2H_3O_2$ is 52.6 per cent ionized at 18°. What is the gram-ion concentration of the $C_2H_3O_2^-$ ion?

15. Calculate the gram-ion concentration of Mg^{++} ion in a 0.1 *M* $MgSO_4$ solution, which is 40.3 per cent ionized at 18° C.

Ans. 4.0×10^{-2}.

16. From the following data calculate the molar strengths of the following solutions:

(*a*) Concentrated HCl, sp. gr. 1.19, containing 37.23 per cent HCl (by weight).

Ans. (*a*) 12.1 *M*.

(*b*) Concentrated HNO_3, sp. gr. 1.42, containing 69.77 per cent HNO_3 (by weight).

Ans. (*b*) 15.7 *M*.

(*c*) Concentrated H_2SO_4, sp. gr. 1.84, containing 95.60 per cent H_2SO_4 (by weight).

Ans. (*c*) 18.0 *M*.

17. (*a*) Concentrated ammonium hydroxide solution has a specific gravity of 0.900 and contains 28.33 per cent NH_3 by weight. Calculate its molar concentration. (*b*) If concentrated ammonium hydroxide solution is diluted 1 : 2 with water, what would be the molarity of the diluted solution?

Ans. (*a*) 15.0 *M*.
(*b*) 5.0 *M*.

18. Calculate the gram-ion amount of Cl^- ion required to react with 10 ml. of a lead nitrate solution containing 10 mg. of Pb^{++} per ml.

Ans. 9.6×10^{-4}.

19. What volume of 6 *M* NH_4OH would be required to precipitate the

aluminum as $Al(OH)_3$ in 25 ml. of a "test solution" containing 10 mg. Al^{+++} ion per ml.?

Ans. 4.6 ml.

20. How many milliliters of concentrated hydrochloric acid solution are required to prepare 100 ml. of 0.3 *M* HCl? Concentrated HCl has a specific gravity of 1.19 and contains 37.23 per cent HCl by weight.

Ans. 2.5 ml.

CHAPTER XIV

EQUILIBRIA CALCULATIONS

The calculations in Chapters XIV–XIX are based upon applications of the law of chemical equilibrium to various types of equilibria. As previously stated this law has a wide application to a great variety of reversible systems, for example, the distribution of a solute between two immiscible solvents, reactions between molecules of organic compounds, reactions between gas molecules, equilibria between dissolved molecules and their ions, complex ion equilibria, hydrolysis, equilibria between precipitates and their saturated solutions, equilibria between oxidizing and reducing agents, etc. The law of chemical equilibrium is one of the most important chemical principles. In qualitative analysis it is applied to a number of important ionic equilibria. The calculations involved in a study of these various types of equilibria are simple and are similar, but as a matter of convenience, problems illustrative of each type will be treated separately in the following pages. The equilibria discussed are:

I. Ionization equilibria, in which K is called the **ionization constant** and may be written $K_{(\text{ion})}$.

II. Equilibria between ions of saturated solutions of slightly soluble compounds, in which K is called the **solubility-product constant** and may be written $K_{\text{s.p.}}$

III. Complex-ion equilibria, in which K is called an **instability constant,** or a **complex dissociation constant,** and may be written $K_{(\text{instab.})}$.

IV. Hydrolysis equilibria, in which K is called an **hydrolysis constant** and may be written $K_{(\text{hyd.})}$.

V. Oxidation-reduction equilibria, in which K is called an **oxidation-reduction constant** and may be written $K_{(\text{ox-red.})}$.

IONIZATION EQUILIBRIA

Acids and Bases. According to the electrolytic dissociation theory, an acid is a substance which dissociates in aqueous solution into hydrogen ions and anions, whereas a base yields hydroxyl ions and cations:

$$HA \rightleftharpoons H^+ + A^- \qquad \text{(Acid)} \qquad (1)$$

$$BOH \rightleftharpoons B^+ + OH^- \qquad \text{(Base)} \qquad (2)$$

According to this definition, a solution of an acid contains free hydrogen ions, hydrogen nuclei, or protons. But these elementary positive charges cannot exist as such in a solution and will combine with the solvent, e.g., water:

$$H^+ + H_2O \rightleftharpoons OH_3^+ \qquad (3)$$

Hence, by combining equations (1) and (3) it will be seen that the dissociation of an acid in water should be represented as follows:

$$HA + H_2O \rightleftharpoons OH_3^+ + A^- \qquad (4)$$

However, so long as we are dealing with aqueous solutions it is immaterial whether the dissociation of an acid is represented by equation (1) or (4), provided we remember that all hydrogen ions are present in the hydrated form as **Oxonium ions,** OH_3^+ (also called **hydronium ion,** or **hydroxonium ion**).

Brønsted [1] has pointed out that the classical definition of acids and bases is not rational and that any substance which can split off protons should be called an acid, whereas one which has the property of combining with protons to form an acid should be called a base. Hence, an acid always forms a conjugated system with a base, as indicated by the following equation:

$$\underset{\text{Acid}}{A} \rightleftharpoons \underset{\text{Base}}{B} + H^+$$

It will be noted that water behaves both as an acid and as a base. Water is a base because it can add a hydrogen ion to form

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[1] Brønsted, *Chem. Rev.*, 5, 231 (1928); see also, Kolthoff, "The Colorimetric and Potentiometric Determination of *p*H," p. 5, John Wiley & Sons, New York, 1931.

oxonium ion (equation 3); it is an acid because it can lose a hydrogen ion to form hydroxyl ion:

$$\underset{\text{Acid}}{H_2O} \rightleftharpoons H^+ + \underset{\text{Base}}{OH^-}$$

Brønsted's conceptions are of invaluable importance in a general treatment of acid-base properties. However, since only systems in water are discussed in this elementary treatise, we will use the classical expressions with which the student is already familiar.

Case 10. Given the molarity of a weak acid or base and its degree of ionization: Calculate the ionization constant.

Example 1. A 0.1 M solution of ammonium hydroxide is 1.33 per cent ionized at 25° C. Calculate the ionization constant of NH_4OH.

Ammonium hydroxide ionizes according to the following reaction:

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

When equilibrium is reached at 25° C., 1.33 per cent of the 0.1 M NH_4OH has ionized. Therefore, in 1 liter of the solution the concentrations are:

$$\begin{aligned} NH_4^+ \text{ ion} &= 0.1 \times 0.0133 = 0.00133 \text{ gram-ion.} \\ OH^- \text{ ion} &= 0.1 \times 0.0133 = 0.00133 \text{ gram-ion.} \\ \text{Non-ionized } NH_4OH &= 0.1 \times 0.9867 = 0.09867 \text{ gram-mol.} \end{aligned}$$

The equilibrium equation is

$$\frac{C_{NH_4^+} \times C_{OH^-}}{C_{NH_4OH}} = K_{(\text{ion})}$$

Substituting the concentration values, we have,

$$\frac{(0.1 \times 0.0133) \times (0.1 \times 0.0133)}{(0.1 \times 0.9867)} = K_{(\text{ion})} = 0.0_418 \text{ or } 1.8 \times 10^{-5}$$

Hence, the ionization constant for NH_4OH is 1.8×10^{-5}. The value of $K_{(\text{ion})}$ is independent of the concentration of the ammonium hydroxide and is a numerical expression of the tendency of ammonium hydroxide to ionize. The $K_{(\text{ion})}$ is a characteristic physical property of ammonium hydroxide just as is its specific gravity or its boiling-point.

In a similar manner the law of chemical equilibrium can be applied to all weak acids and bases and their respective ionization constants obtained. Should the values for K, as calculated for different concentrations, not be the same or very nearly the same, then the mass-action law is not applicable to that particular acid or base. Of course, a definite numerical value for K can be obtained for all electrolytes by simply substituting in the equilibrium ratio the values for the concentrations of the ions and the un-ionized molecules (each ion concentration raised to a power equal to the number of the respective ions formed by the ionization of one molecule of the compound). But the fact that a definite numerical value can thus be calculated for K does not make it a **constant.** Only when this value remains sensibly the same for all concentrations can it be a real ionization constant.

The numerical values of the ionization constants of a number of weak acids and bases are given in Table VIII. By an inspection

TABLE VIII

IONIZATION CONSTANTS OF SOME WEAK ACIDS AND BASES

Compound	Ionization	Ionization Constant *
Acid		
Acetic acid..............	$HC_2H_3O_2 \rightleftharpoons H^+ + C_2H_3O_2^-$	1.8×10^{-5}
Arsenious acid...........	$HAsO_2 \rightleftharpoons H^+ + AsO_2^-$	6×10^{-10}
Arsenic acid, primary.....	$H_3AsO_3 \rightleftharpoons H^+ + H_2AsO_4^-$	5×10^{-3}
secondary............	$H_2AsO_4^- \rightleftharpoons H^+ + HAsO_4^{=}$	4×10^{-5}
tertiary..............	$HAsO_4^{=} \rightleftharpoons H^+ + AsO_4^{\equiv}$	6×10^{-10}
Boric acid, primary.......	$H_3BO_3 \rightleftharpoons H^+ + H_2BO_3^-$	6.6×10^{-10}
Carbonic acid, primary....	$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$	3×10^{-7}
secondary............	$HCO_3^- \rightleftharpoons H^+ + CO_3^{=}$	4×10^{-11}
Formic acid..............	$HCHO_2 \rightleftharpoons H^+ + CHO_2^-$	2×10^{-4}
Hydrocyanic acid.........	$HCN \rightleftharpoons H^+ + CN^-$	7×10^{-10}
Hydrogen sulfide, primary.	$H_2S \rightleftharpoons H^+ + HS^-$	9×10^{-8}
secondary............	$HS^- \rightleftharpoons H^+ + S^{=}$	1.2×10^{-15}
Nitrous acid.............	$HNO_2 \rightleftharpoons H^+ + NO_2^-$	4×10^{-4}
Oxalic acid, primary......	$H_2C_2O_4 \rightleftharpoons H^+ + HC_2O_4^-$	3.8×10^{-2}
secondary............	$HC_2O_4^- \rightleftharpoons H^+ + C_2O_4^{=}$	6.1×10^{-5}
Phosphoric acid, primary..	$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$	1.1×10^{-2}
secondary............	$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{=}$	7.5×10^{-8}
tertiary..............	$HPO_4^{=} \rightleftharpoons H^+ + PO_4^{\equiv}$	5×10^{-13}
Sulfuric acid, secondary...	$HSO_4^- \rightleftharpoons H^+ + SO_4^{=}$	3×10^{-2}
Sulfurous acid, primary...	$H_2SO_3 \rightleftharpoons H^+ + HSO_3^-$	1.7×10^{-2}
secondary............	$HSO_3^- \rightleftharpoons H^+ + SO_3^{=}$	1×10^{-7}
Base		
Ammonium hydroxide....	$NH_4OH \rightleftharpoons NH_4^+ + OH^-$	1.75×10^{-5}
Silver hydroxide..........	$AgOH \rightleftharpoons Ag^+ + OH^-$	1.1×10^{-4}

* Room temperature.

of the equilibrium equation it will be evident that, for equivalent solutions of all weak mono-basic acids and mono-acidic bases, the numerical value for K will be greater, the greater the degree of ionization. Hence the ionization constant is a measure of the strength of an acid or base.

The equilibrium equation of all weak electrolytes which upon ionization yield only one cation and one anion for each molecule dissociated can be simplified by factoring out the molarity (see example 1 above). If the degree of ionization (expressed as a decimal fraction) be represented by α, the fraction of un-ionized solute by $1 - \alpha$, and the molarity of the solute by M, the equation becomes

$$\frac{(M \times \alpha) \times (M \times \alpha)}{M(1 - \alpha)} = K_{(\text{ion})}$$

$$\frac{M\alpha^2}{1 - \alpha} = K_{(\text{ion})}$$

or

$$M\left(\frac{\alpha^2}{1 - \alpha}\right) = K_{(\text{ion})}$$

The equilibrium equation expressed in this form is called the Ostwald dilution law or the Ostwald dilution formula (see page 90). By using this equation the calculation of ionization constants is simplified. It is obvious that, if the values of any two of the three quantities in the equation are known, the third can be calculated.

Example 2. Calculate the ionization constant of ammonium hydroxide by use of the Ostwald dilution formula. Given the molarity and degree of ionization of ammonium hydroxide. By experiment 0.1 M NH_4OH is found to be 1.33 per cent ionized at 25° C.

$$M = 0.1 \quad \text{and} \quad \alpha = 0.0133$$

Substituting these values in the Ostwald dilution formula and solving, we have

$$0.1\left(\frac{(0.0133)^2}{1 - 0.0133}\right) = K_{(\text{ion})}$$

$$K_{(\text{ion})} = 1.8 \times 10^{-5}$$

Case 11. Given the degree of ionization and the ionization constant of a weak acid or base. Calculate the molarity.

Example. What is the molarity of an acetic acid solution which is 1.34 per cent ionized, the $K_{(\text{ion})}$ of $HC_2H_3O_2$ being 1.8×10^{-5}?

Substituting in the Ostwald dilution formula and solving,

$$M\left(\frac{(0.0134)^2}{1 - 0.0134}\right) = 1.8 \times 10^{-5}$$

$$M = 0.1$$

Hence, the acetic acid solution is 0.1 *M*.

Case 12. Given the molarity and the ionization constant of a weak acid or base. Calculate the degree of ionization and the ion concentration.

Example. What is the degree of ionization of a 0.1 *M* solution of formic acid, the $K_{(\text{ion})}$ of $HCHO_2$ being 2×10^{-4}? What is the H^+ ion concentration of the solution?

Substituting in the Ostwald equation and solving,

$$0.1\left(\frac{\alpha^2}{1 - \alpha}\right) = 2 \times 10^{-4}$$

Since α in the denominator is so small compared with 1, it can be dropped without introducing an appreciable error. Thus we avoid a quadratic equation.

$$0.1\alpha^2 = 2 \times 10^{-4}$$

$$\alpha^2 = 2 \times 10^{-3}$$

$$\alpha^2 = 20 \times 10^{-4}$$

$$\alpha = 4.5 \times 10^{-2} \text{ or } 4.5 \text{ per cent}$$

The 0.1 *M* formic acid is 4.5 per cent ionized. Hence the H^+ ion concentration is $0.1 \times 0.045 = 0.0045$ gram-ion per liter.

This problem may also be solved as follows:

Let x = the concentration of H^+ ion. In a pure solution of formic acid the $C_{H^+} = C_{CHO_2^-}$, and hence x will also equal the CHO_2^- ion concentration. Since x gram-ions of H^+ and x gram-ions of CHO_2^- came from the complete ionization of x mols of $HCHO_2$, the concentration of un-ionized $HCHO_2$ in a 0.1 *M* solution is $0.1 - x$. Substituting these values in the equilibrium equation we get

$$\frac{x \times x}{0.1 - x} = 2 \times 10^{-4}$$

In this equation, x in the denominator is so small compared with 0.1 that it can be dropped without introducing an appreciable error and thus avoid solving a quadratic equation.

$$\frac{x^2}{0.1} = 2 \times 10^{-4}$$

$$x^2 = 2 \times 10^{-5}$$

$$x^2 = 20 \times 10^{-6}$$
$$x = 4.5 \times 10^{-3}$$

Hence the H$^+$ ion concentration is 4.5×10^{-3} or 0.0045 gram-ion per liter.

Solving the equilibrium equation as a quadratic[2] we have

$$\frac{x^2}{0.1 - x} = 2 \times 10^{-4} \tag{1}$$

Cross multiplying and rearranging,

$$x^2 + 2 \times 10^{-4}x - 2 \times 10^{-5} = 0 \tag{2}$$

Solving for x in the general quadratic equation, $ax^2 + bx + c = 0$, we obtain

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \tag{3}$$

Substituting in (3) the terms in (2), we get

$$\begin{aligned}
x &= \frac{-2 \times 10^{-4} \pm \sqrt{(2 \times 10^{-4})^2 - 4(-2 \times 10^{-5})}}{2} \\
&= \frac{-2 \times 10^{-4} \pm \sqrt{(4 \times 10^{-8}) + (8 \times 10^{-5})}}{2} \\
&= \frac{-2 \times 10^{-4} \pm \sqrt{8004 \times 10^{-8}}}{2} \\
&= \frac{-2 \times 10^{-4} \pm 90 \times 10^{-4}}{2} \\
&= -1 \times 10^{-4} \pm 45 \times 10^{-4} \\
&= 44 \times 10^{-4} \quad \text{or} \quad -46 \times 10^{-4}
\end{aligned}$$

Mathematically, either answer is correct, but as the H$^+$ ion concentration cannot have a negative value, the negative result is discarded and 44×10^{-4} or 4.4×10^{-3} gram-ion per liter is taken as the concentration of the H$^+$ ion. Note that this value differs very little from 4.5×10^{-3} which was the concentration obtained by the approximation equation.

Polybasic Acids. Acids which contain two or more ionizable hydrogen atoms are called polybasic acids. Such acids ionize in stages. Thus H_2S and H_2CO_3 are dibasic acids and ionize in two stages. Tribasic acids, e.g., H_3AsO_4 and H_3PO_4, ionize in three stages. The ionization stages of these acids are shown by the following reactions:

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[2] If the student is not familiar with the solution of a quadratic equation, he should consult a textbook on algebra.

$H_2S \rightleftharpoons H^+ + HS^-$ (primary)

$HS^- \rightleftharpoons H^+ + S^=$ (secondary)

$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$ (primary)

$HCO_3^- \rightleftharpoons H^+ + CO_3^=$ (secondary)

$H_3AsO_4 \rightleftharpoons H^+ + H_2AsO_4^-$ (primary)

$H_2AsO_4^- \rightleftharpoons H^+ + HAsO_4^=$ (secondary)

$HAsO_4^= \rightleftharpoons H^+ + AsO_4^\equiv$ (tertiary)

$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$ (primary)

$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^=$ (secondary)

$HPO_4^= \rightleftharpoons H^+ + PO_4^\equiv$ (tertiary)

In polybasic acids, the second stage ionization takes place to a very much less extent than the first; the third stage very much less than the second; and so on. See Table VIII for a comparison of the ionization constants for the different stages of ionization. These constants are obtained by applying the law of chemical equilibrium to each ionization stage. For the above-mentioned polybasic acids we write the following equations:

H_2S

First stage: $$\frac{C_{H^+} \times C_{HS^-}}{C_{H_2S}} = K_1 \qquad (1)$$

Second stage: $$\frac{C_{H^+} \times C_{S^=}}{C_{HS^-}} = K_2 \qquad (2)$$

H_2CO_3

First stage: $$\frac{C_{H^+} \times C_{HCO_3^-}}{C_{H_2CO_3}} = K_1 \qquad (1)$$

Second stage: $$\frac{C_{H^+} \times C_{CO_3^=}}{C_{HCO_3^-}} = K_2 \qquad (2)$$

H_3AsO_4

First stage: $$\frac{C_{H^+} \times C_{H_2AsO_4^-}}{C_{H_3AsO_4}} = K_1 \qquad (1)$$

Second stage: $$\frac{C_{H^+} \times C_{HAsO_4^=}}{C_{H_2AsO_4^-}} = K_2 \qquad (2)$$

Third stage: $$\frac{C_{H^+} \times C_{AsO_4^{\equiv}}}{C_{HAsO_4^{=}}} = K_3 \qquad (3)$$

H_3PO_4
First stage: $$\frac{C_{H^+} \times C_{H_2PO_4^-}}{C_{H_3PO_4}} = K_1 \qquad (1)$$

Second stage: $$\frac{C_{H^+} \times C_{HPO_4^{=}}}{C_{H_2PO_4^-}} = K_2 \qquad (2)$$

Third stage: $$\frac{C_{H^+} \times C_{PO_4^{\equiv}}}{C_{HPO_4^{=}}} = K_3 \qquad (3)$$

The Hydrogen Sulfide Equilibrium. The solubility of hydrogen sulfide gas in water has been found to be 3.38 g. per liter at 25° C. and 760 mm. pressure. This corresponds to a molar concentration of about 0.1. By experiment, the concentration of H^+ ion and of HS^- ion in a liter of water saturated with H_2S at 25° C. has been found to be 9.5×10^{-5} gram-ion each, and the $S^{=}$ ion concentration 1.2×10^{-15} gram-ion. Substituting these values in the equilibrium ratios for the primary and secondary ionizations of hydrogen sulfide, we get

$$\frac{(9.5 \times 10^{-5}) \times (9.5 \times 10^{-5})}{0.1} = K_1 = 9.0 \times 10^{-8}$$

$$\frac{(9.5 \times 10^{-5}) \times (1.2 \times 10^{-15})}{9.5 \times 10^{-5}} = K_2 = 1.2 \times 10^{-15}$$

Note that $C_{S^{=}}$ is numerically equal to K_2. This is true since the values of C_{H^+} and C_{HS^-} as derived from the primary ionization are practically equal and at equilibrium they must each have a value which will satisfy both equilibrium constants. Of course the values of C_{H^+} and of C_{HS^-} will be different for different concentrations of H_2S, but as they are practically equal they will cancel out when substituted in the equilibrium ratio for the secondary ionization. This relationship holds true for all weak dibasic acids, namely: the concentration of the divalent ion resulting from the secondary ionization is numerically equal to the secondary ionization constant.

Combining the equations for the primary and secondary ionization constants, we obtain

$$\frac{C_{\text{H}^+} \times C_{\text{HS}^-}}{C_{\text{H}_2\text{S}}} \times \frac{C_{\text{H}^+} \times C_{\text{S}^=}}{C_{\text{HS}^-}} = K_1 \times K_2$$

$$\frac{C^2_{\text{H}^+} \times C_{\text{S}^=}}{C_{\text{H}_2\text{S}}} = K_{(\text{ion})}$$

Substituting the concentration values in this equation, we get

$$\frac{(9.5 \times 10^{-5})^2 \times (1.2 \times 10^{-15})}{0.1} = 1.1 \times 10^{-22} = K_{(\text{ion})}$$

Since in a saturated solution of H_2S the ionization is so extremely small, we may consider the concentration of undissociated H_2S to be 0.1 *M*. Hence, we may obtain a modified equation which will simplify calculations involving the H_2S equilibrium.

$$C^2_{\text{H}^+} \times C_{\text{S}^=} = 1.1 \times 10^{-22} \times 0.1 = 1.1 \times 10^{-23} = K_{(\text{H}_2\text{S})}$$

An inspection of this modified equation shows that the $S^=$ ion concentration is inversely proportional to the square of the H^+ ion concentration. For example, if we should double the H^+ ion concentration (by adding any acid, say HNO_3), we would simultaneously reduce the $S^=$ concentration to one-fourth of its original value. This equation used in conjunction with solubility-product equations for the metallic sulfides enables us to make many useful analytical calculations as will be shown in the examples which follow.

It was stated above that $C_{\text{S}^=}$ is numerically equal to the secondary ionization constant 1.2×10^{-15}. Substituting this value in the modified or ion-product H_2S equation, we get

$$C^2_{\text{H}^+} = \frac{1.1 \times 10^{-23}}{1.2 \times 10^{-15}} = 0.917 \times 10^{-8}$$

$$C_{\text{H}} = \sqrt{91.7 \times 10^{-10}} = 9.5 \times 10^{-5}$$

Hence a liter of water saturated with H_2S at 25° C. and 760 mm. pressure contains 9.5×10^{-5} gram-ion of H^+ ion and 1.2×10^{-15} gram-ion of $S^=$ ion. If the equation $H_2S \rightleftharpoons 2H^+ + S^=$ correctly expressed the ionization of H_2S in pure water, then the concentration of H^+ ion should be twice that of the $S^=$ ion. Obviously this is not true. The primary ionization of H_2S is so very much greater than the secondary ionization that obviously the equation $H_2S \rightleftharpoons 2H^+ + S^=$ does not express the H_2S ionization correctly.

Case 13. Calculations involving polybasic acids.

Example 1. What is the approximate H^+ ion concentration of a $0.05M$ H_2S solution?

Since the secondary ionization is so extremely small as compared with the primary, the H^+ ion concentration of weak dibasic acids is derived almost entirely from the primary ionization. In other words, as far as the H^+ ion is concerned, the weak dibasic acids may be considered as monobasic acids.

In example 1, let x = H^+ ion concentration. x will also equal the HS^- ion concentration. Substituting in the equilibrium equation for the primary ionization, we get

$$\frac{x \times x}{0.05} = 9.0 \times 10^{-8}$$

$$x^2 = 0.45 \times 10^{-8} = 45 \times 10^{-10}$$

$$x = 6.7 \times 10^{-5} \text{ mol per liter}$$

Example 2. The secondary ionization constant, K_2, of oxalic acid is 6.1×10^{-5}. What is the $C_2O_4^=$ ion concentration?

Oxalic acid ionizes in two stages as follows:

$$H_2C_2O_4 \rightleftharpoons H^+ + HC_2O_4^- \qquad (1)$$

$$HC_2O_4^- \rightleftharpoons H^+ + C_2O_4^= \qquad (2)$$

The equilibrium ratios for the two equilibria are

$$\frac{C_{H^+} \times C_{HC_2O_4^-}}{C_{H_2C_2O_4}} = K_1 \qquad (1)$$

$$\frac{C_{H^+} \times C_{C_2O_4^=}}{C_{HC_2O_4^-}} = K_2 = 6.1 \times 10^{-5} \qquad (2)$$

Since C_{H^+} and $C_{HC_2O_4^-}$ are practically equal, they cancel out in equation (2). Hence,

$$C_{C_2O_4^=} = 6.1 \times 10^{-5} \text{ mol per liter}$$

PROBLEMS

1. A 0.1 M solution of $HC_2H_3O_2$ is 1.34 per cent ionized at 18° C. Calculate the ionization constant, K_a, of $HC_2H_3O_2$.

Ans. 1.82×10^{-5}.

2. What is the K_a of $HCHO_2$ which is 13.4 per cent ionized at 25° C. in 0.01 M solution?

Ans. 2.1×10^{-4}.

3. Calculate the value of the ionization constant, K_b, of NH_4OH, knowing that it is 1.31 per cent ionized at 18° C. in 0.1 *M* solution.

Ans. 1.74×10^{-5}.

4. By calculating the value of K_a at the following different concentrations at 25°, show that $HC_2H_3O_2$ has a true ionization constant:

(*a*) 1.0 *M* $HC_2H_3O_2$ is 0.4 per cent ionized.

Ans. (*a*) 1.6×10^{-5}.

(*b*) 0.01 *M* $HC_2H_3O_2$ is 4.2 per cent ionized.

Ans. (*b*) 1.8×10^{-5}.

(*c*) 0.001 *M* $HC_2H_3O_2$ is 12.8 per cent ionized.

Ans. (*c*) 1.9×10^{-5}.

5. Compare the values of K_b for NH_4OH at 25° and at the following dilutions:

(*a*) 1.0 *M* NH_4OH is 0.42 per cent ionized.

Ans. (*a*) 1.77×10^{-5}.

(*b*) 0.01 *M* NH_4OH is 4.2 per cent ionized.

Ans. (*b*) 1.84×10^{-5}.

(*c*) 0.001 *M* NH_4OH is 12.5 per cent ionized.

Ans. (*c*) 1.79×10^{-5}.

6. Strong electrolytes are not characterized by an ionization constant. To illustrate this, calculate the value for *K* at 18° for NaOH at the following concentrations:

(*a*) 0.1 *M* (90.5 per cent ionized).	*Ans.* (*a*) 0.86.
(*b*) 0.01 *M* (93.3 per cent ionized).	(*b*) 0.13.
(*c*) 0.001 *M* (97.1 per cent ionized).	(*c*) 0.033.

7. Show that HNO_3 has no true ionization constant. At 18° C., the percentage ionization of 0.1 *M*, 0.01 *M*, and 0.001 *M* HNO_3 is 92.0, 96.9, and 99.0, respectively.

8. The percentage ionization of K_2SO_4 at 18° C. is 67.3, 83.2, and 93.7 in concentrations of 0.1 *M*, 0.01 *M*, and 0.001 *M*, respectively. Does K_2SO_4 have an ionization constant?

9. Calculate the molar strength of a solution of $HC_2H_3O_2$ which is 5.0 per cent ionized. The K_a for $HC_2H_3O_2$ is 1.85×10^{-5} at 25° C.

Ans. 0.007 *M*.

10. What is the concentration of a solution of NH_4OH which is 5 per cent ionized? 10 per cent ionized? K_b for NH_4OH is 1.75×10^{-5}.

Ans. 0.0067 *M*, 0.0016 *M*.

11. The K_a for HCN is 7.2×10^{-10}. Calculate the molarity of an HCN solution which is 0.01 per cent ionized.

Ans. 0.072 *M*.

12. Calculate the strength of a solution of HNO_2 which is 3.0 per cent ionized. K_a for HNO_2 is 4×10^{-4}.

Ans. 0.43 *M*.

13. What is the degree of ionization of a 0.15 M solution of $HC_2H_3O_2$, the K_a being 1.85×10^{-5}? What is the concentration of the non-ionized $HC_2H_3O_2$?

Ans. 1.1×10^{-2}, 0.148 M.

14. The K_b for NH_4OH is 1.75×10^{-5}. Calculate the percentage ionization in a 0.2 M solution of NH_4OH.

Ans. 93.

15. Calculate the concentration of H^+ in a liter of 0.1 M $HC_2H_3O_2$. K_a for $HC_2H_3O_2$ is 1.85×10^{-5}.

Ans. 1.4×10^{-3} gram-ion per l.

Common-Ion Effect. The effect, on the ionization equilibrium of a weak electrolyte, of adding a common ion has many applications in analytical chemistry. Use is made of it (1) in controlling the H^+ ion and OH^- ion concentrations of solutions in which precipitation reactions are carried out, (2) in decreasing the solubility of a slightly soluble compound, and (3) in preventing the precipitation of certain substances.

Case 14. Calculations involving the addition of a common-ion.

Example 1. Calculate the H^+ ion concentration in 1 liter of 0.1 M $HC_2H_3O_2$ solution to which have been added 7.7 g. of $NH_4C_2H_3O_2$ which ionizes to the extent of 84 per cent; 0.1 M $HC_2H_3O_2$ is 1.34 per cent ionized and its $K_{(\text{ion})} = 1.82 \times 10^{-5}$.

Acetic acid ionizes as follows:

$$HC_2H_3O_2 \rightleftharpoons H^+ + C_2H_3O_2^-$$

Before $NH_4C_2H_3O_2$ is added:

$$C_{H^+} = 0.1 \times 0.0134 = 0.00134 \text{ gram-ion per liter}$$
$$C_{C_2H_3O_2^-} = 0.1 \times 0.0134 = 0.00134 \text{ gram-ion per liter}$$
$$C_{HC_2H_3O_3} = 0.1 - 0.00134 = 0.09866 \text{ gram-mol per liter}$$

After $NH_4C_2H_3O_2$ is added:

$$\text{Mol. wt. } NH_4C_2H_3O_2 = 77$$
$$\therefore \quad 7.7 \text{ g. } NH_4C_2H_3O_2 = 0.1 \text{ mol}$$

0.1 M $NH_4C_2H_3O_2$ is 84 per cent ionized.

Therefore it yields

$$0.1 \times 0.84 = 0.084 \text{ gram-ion of } C_2H_3O_2^- \text{ ion}$$
$$\text{Total } C_{C_2H_3O_2^-} = 0.00134 + 0.084 = 0.08534 \text{ gram-ion per liter}$$

The increase in the $C_2H_3O_2^-$ ion concentration means that more collisions per second of H^+ ions with $C_2H_3O_2^-$ ions will occur. This results in the formation of more $HC_2H_3O_2$ molecules per second and hence maintains a higher concentration of non-ionized $HC_2H_3O_2$ than was present before the

$NH_4C_2H_3O_2$ was added. But the non-ionized $HC_2H_3O_2$ can increase only to 0.1 M as a maximum. The addition of $NH_4C_2H_3O_2$ increases the $C_2H_3O_2^-$ ion concentration to $\frac{0.08534}{0.00134}$ or 64 times its original value. Therefore the number of collisions per second between H^+ ions and $C_2H_3O_2^-$ ions will be 64 times as great. As a first approximation of the increase in non-ionized $HC_2H_3O_2$ we have $\frac{63}{64} \times 0.00134 = 0.00132$ mol per liter. The total $C_{HC_2H_3O_2}$ will now be $0.09866 + 0.00132 = 0.09998$ mol per liter. Substituting the values for $C_{C_2H_3O_2^-}$ and $C_{HC_2H_3O_2}$ in the equilibrium equation, we get

$$\frac{C_{H^+} \times 0.08534}{0.09998} = 1.82 \times 10^{-5}$$

$$C_{H^+} = \frac{0.09998 \times 1.82 \times 10^{-5}}{0.08534} = 2.1 \times 10^{-5} \text{ gram-ion per liter}$$

Hence, the addition of 7.7 g. (0.1 mol) of $NH_4C_2H_3O_2$ to a liter of 0.1 M $HC_2H_3O_2$ caused a lowering of the H^+ ion concentration from 1.34×10^{-3} gram-ion per liter to 2.1×10^{-5} gram-ion per liter, i.e., a lowering to $\frac{2.1 \times 10^{-5}}{1.34 \times 10^{-3}}$ or $\frac{1}{64}$ of its original value.

Example 2. Calculate the H^+ ion concentration in example 1 by quadratics.

Let x = the decrease in H^+ ion and $C_2H_3O_2^-$ ion concentrations due to formation of non-ionized $HC_2H_3O_2$. The increase in non-ionized $HC_2H_3O_2$ concentration will also equal x.

From example 1,

$$\begin{aligned} \text{Original } C_{H^+} &= 0.00134 \text{ gram-ion per liter} \\ \text{Total } C_{C_2H_3O_2^-} &= 0.08534 \text{ gram-ion per liter} \\ \text{Original } C_{HC_2H_3O_2} &= 0.09866 \text{ gram-mol per liter} \end{aligned}$$

The final or equilibrium concentrations will be:

$$\begin{aligned} C_{H^+} &= 0.00134 - x \\ C_{C_2H_3O_2^-} &= 0.08534 - x \\ C_{HC_2H_3O_2} &= 0.09866 + x \end{aligned}$$

Substituting these values in the equilibrium equation,

$$\frac{(0.00134 - x) \times (0.08534 - x)}{0.09866 + x} = 1.82 \times 10^{-5}$$

$$(114.3 \times 10^{-6}) - 0.08668x + x^2 = (1.7956 \times 10^{-6}) + (1.82 \times 10^{-5})x$$

Rearranging

$$x^2 - 0.086698x + (1.125 \times 10^{-4}) = 0$$

Substituting in the general quadratic formula,

$$x = \frac{0.086698 \pm \sqrt{(0.086698)^2 - 4(1.125 \times 10^{-4})}}{2}$$

$$= \frac{0.086698 \pm \sqrt{(75.168 \times 10^{-4}) - (4.500 \times 10^{-4})}}{2}$$

$$= \frac{0.086698 \pm \sqrt{0.0070668}}{2}$$

$$= \frac{0.086698 \pm 0.08406}{2}$$

$$= 0.085379 \text{ or } 0.001319$$

If 0.085379 be taken as the value for x, then $0.08534 - x$ will have a negative value. Hence, the value to be used is 0.001319. This is the amount by which the H^+ ion and $C_2H_3O_2^-$ ion concentrations are decreased and the $HC_2H_3O_2$ concentration is increased. Therefore at equilibrium, the concentrations will be:

$$C_{H^+} = 0.00134 - 0.001319 = 2.1 \times 10^{-5} \text{ gram-ion per liter}$$
$$C_{C_2H_3O_2^-} = 0.08534 - 0.001319 = 0.08402 \text{ gram-ion per liter}$$
$$C_{HC_2H_3O_2} = 0.09866 + 0.001319 = 0.09998 \text{ gram-mol per liter}$$

Hence, the addition of 0.1 mol of $NH_4C_2H_3O_2$ to 1 liter of 0.1 *M* $HC_2H_3O_2$ lowered the H^+ ion concentration from an initial value of 1.34×10^{-3} gram-ion per liter to 2.1×10^{-5} gram-ion per liter.

Example 3. Calculate the H^+ concentration in example 1 by the method of approximation.

The use of a quadratic equation in calculating the common-ion effect is very tedious, and except for work requiring precise values, it is possible to simplify the calculation greatly by making two approximations. First, the initial $C_2H_3O_2^-$ ion concentration (0.08534 g. per liter) and the final concentration (0.08402 g. per liter) differ so little that we may take as an approximation the $C_2H_3O_2^-$ ion concentration furnished by the $NH_4C_2H_3O_2$, i.e., 0.084 g. per liter. Second, the concentration of non-ionized $HC_2H_3O_2$ after the addition of the $NH_4C_2H_3O_2$ is 0.09998 mol per liter, which is very nearly that of the original molarity. Hence, the concentration of non-ionized acid may be taken as equal to the molarity of the acid, i.e., 0.1 *M*.

Let $x = C_{H^+}$ at equilibrium after 0.1 mol of $NH_4C_2H_3O_2$ has been added. Substituting in the equilibrium equation and solving for x,

$$\frac{x \times 0.084}{0.1} = 1.82 \times 10^{-5}$$
$$0.084x = 1.82 \times 10^{-6}$$
$$x = 2.17 \times 10^{-5}$$
$$= 2.2 \times 10^{-5} \text{ gram-ion per liter}$$

Example 4. Calculate the $S^=$ ion concentration in a 0.3 *M* HNO_3 solution saturated with H_2S at room temperature and under atmospheric pressure. Pure 0.3 *M* HNO_3 is about 90 per cent ionized at room temperature.

$$C^2_{H^+} \times C_{S^=} = 1.1 \times 10^{-23}$$

A pure aqueous solution of H_2S saturated at room temperature and under atmospheric pressure contains 9.5×10^{-5} gram-ion of H^+ ion and 1.2×10^{-15} gram-ion of $S^{=}$ ion (see page 127). But in 0.3 M solution of a strong acid, such as HNO_3 or HCl, the H^+ ion concentration and simultaneously the $S^{=}$ ion concentration are very greatly decreased. Since the H^+ ion concentration derived from the dissociation of the H_2S is so small as compared to that from the ionization of the 0.3 M HNO_3, it may be disregarded without introducing an appreciable error in the following calculation.

$$C_{H^+} \text{ in } 0.3\ M\ HNO_3 = 0.3 \times 0.90 = 0.27 \text{ gram-ion per liter}$$

$$C_{S^=} = \frac{1.1 \times 10^{-23}}{C^2_{H^+}} = \frac{1.1 \times 10^{-23}}{(0.27)^2}$$

$$= \frac{1.1 \times 10^{-23}}{7.29 \times 10^{-2}} = 1.5 \times 10^{-22} \text{ gram-ion per liter}$$

Buffer Action. Buffer action is an example of the common-ion effect applied to solutions of weak acids and bases. Thus it is possible to maintain a fairly constant and known H^+ ion or OH^- ion concentration, a condition which is frequently required in analytical procedures. This is accomplished by employing either a mixture of a weak acid and one of its salts (usually the sodium, potassium, or ammonium salt) or a mixture of a weak base and one of its salts. Such mixtures are called buffer mixtures, buffer solutions, or simply buffers. The maintaining of an approximately constant H^+ ion or OH^- ion concentration in a solution containing a weak acid or base is known as buffer action (see page 197). Some commonly used buffer mixtures are: $HCHO_2$—$NaCHO_2$; $HC_2H_3O_2$—$NaC_2H_3O_2$; $HC_2H_3O_2$—$NH_4C_2H_3O_2$; NH_4OH—NH_4Cl; and NH_4OH—NH_4NO_3.

Example 5. In a liter of 0.1 M NH_4OH solution 0.25 mol of solid NH_4Cl is dissolved. Calculate the approximate OH^- ion concentration of the buffer solution; 0.25 M NH_4Cl is about 80 per cent ionized.

$$\underset{20\%}{NH_4Cl} \rightleftharpoons \underset{80\%}{NH_4^+ + Cl^-}$$

Hence in a 0.25 M NH_4Cl solution [3]

$$C_{NH_4^+} = 0.25 \times 0.80 = 0.2 \text{ mol per liter}$$

In 0.1 M NH_4OH,

$$C_{NH_4OH} = 0.1\ M \text{ (approximated)}$$

$$\frac{0.2 \times C_{OH^-}}{0.1} = 1.75 \times 10^{-5}$$

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[3] The small amount of NH_4^+ ion coming from the dissociation of 0.1 M NH_4OH is disregarded in calculating the approximate OH^- ion concentration of the buffer solution.

$$
\begin{aligned}
C_{\mathrm{OH}^-} &= \frac{0.1 \times 1.75 \times 10^{-5}}{0.2} \\
&= \frac{1.75 \times 10^{-6}}{0.2} \\
&= 8.8 \times 10^{-6} \\
&= 9 \times 10^{-6} \text{ gram-ion per liter}^{4}
\end{aligned}
$$

PROBLEMS

1. What is the H^+ ion concentration in a liter of 0.1 M $HC_2H_3O_2$ after enough $NH_4C_2H_3O_2$ has been added to raise the total $C_2H_3O_2^-$ ion concentration to 0.5 M? K_a of $HC_2H_3O_2$ is 1.85×10^{-5}.

Ans. 3.7×10^{-6} gram-ion per l.

2. One-tenth gram-mol of $NaC_2H_3O_2$ is added to a liter of 0.05 M $HC_2H_3O_2$. Calculate the approximate H^+ ion concentration of the solution, assuming the $NaC_2H_3O_2$ to be 77 per cent ionized.

Ans. 1.2×10^{-5} gram-ion per l.

3. Enough NH_4NO_3 is dissolved in a 0.1 M NH_4OH solution to raise the total NH_4^+ ion concentration to 0.5 M. Calculate the approximate OH^- ion concentration of the solution. K_b for NH_4OH is 1.75×10^{-5}.

Ans. 3.5×10^{-6} gram-ion per l.

4. A gram-mol of NH_4Cl is dissolved in a liter of 0.01 M NH_4OH. Calculate the approximate OH^- ion concentration of the solution, assuming the NH_4Cl to be 74 per cent ionized.

Ans. 2.4×10^{-7} gram-ion per l.

5. To a liter of 0.01 M $HC_2H_3O_2$ solution 8.2 grams of $NaC_2H_3O_2$ are added. To what extent is the H^+ ion concentration lowered? Assume that the $NaC_2H_3O_2$ is 77 per cent ionized.

Ans. 99%.

6. How many grams of NH_4Cl must be dissolved in a liter of 1 M NH_4OH in order to reduce the OH^- ion concentration to 0.0001 M? Assume that the NH_4Cl is 75 per cent ionized.

Ans. 12.5 g.

7. Equal volumes of 0.1 M $HC_2H_3O_2$ and 0.1 M $NaC_2H_3O_2$ are mixed. What is the H^+ ion concentration of the resulting solution, assuming the $NaC_2H_3O_2$ to be 84 per cent ionized?

Ans. 2.2×10^{-5} gram-ion per l.

8. Calculate the grams of $NH_4C_2H_3O_2$ that must be dissolved in a liter of 0.01 M $HC_2H_3O_2$ to reduce its H^+ ion concentration to 1×10^{-5} M. Assume that the $NH_4C_2H_3O_2$ is 75 per cent ionized.

Ans. 1.9 g.

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[4] It is suggested that the student repeat the above calculation, using the total NH_4^+ ion concentration, i.e., NH_4^+ furnished by both 0.25 M NH_4Cl and 0.1 M NH_4OH. Compare this result with that obtained in the above calculation. One-tenth M NH_4OH is 1.3 per cent ionized.

9. Compare the buffering effect of adding 0.1 gram-mol of the corresponding ammonium salt to a liter of 1 *M* solution of each of the following acids: HCN, HNO_2, and $HCHO_2$. Assume complete ionization of the ammonium salts.

Ans. (*a*) 7 × 10^{-9} gram-ion H^+ per l.
(*b*) 4 × 10^{-3} gram-ion H^+ per l.
(*c*) 2 × 10^{-3} gram-ion H^+ per l.

10. How many grams of $(NH_4)_2SO_4$ must be added to 100 ml. of 0.1 *M* NH_4OH to lower its OH^- ion concentration to 0.0005 *M*?

Ans. 2.3 × 10^{-2} g.

11. Calculate the $S^=$ ion concentration in an acid solution saturated with H_2S and containing a total H^+ ion concentration of 0.3 *M*. $C^2_{H^+} \times C_{S^=} = 1.1 \times 10^{-23}$.

Ans. 1.2 × 10^{-22} gram-ion per l.

12. If 1.0 ml. of 12 *M* HCl is diluted to 100 ml. with water and saturated with H_2S, what would be the sulfide ion concentration?

Ans. 9.2 × 10^{-22} gram-ion per l.

13. Calculate the H^+ ion and OH^- ion concentration, respectively, in a 0.1 *M* HNO_3 solution which is 96.0 per cent ionized at 25° C. The ion-product constant of water, K_w, is $C_{H^+} \times C_{OH^-} = 1.0 \times 10^{-14}$ at 25° C.

Ans. 9.6 × 10^{-2} gram-ion per l.
1.04 × 10^{-13} gram-ion per l.

14. A 0.1 *M* NaOH solution is 92.9 per cent ionized at 25° C. What are the H^+ ion and OH^- ion concentrations, respectively?

Ans. 9.3 × 10^{-2} gram-ion per l.
1.08 × 10^{-13} gram-ion per l.

15. One hundred milliliters of 0.1 *M* $NaC_2H_3O_2$ are added to 100 ml. of 0.2 *M* $HC_2H_3O_2$. Calculate the approximate H^+ ion concentration of the solution, assuming the $NaC_2H_3O_2$ to be 84 per cent ionized.

Ans. 4.4 × 10^{-5} gram-ion per l.

CHAPTER XV

SOLUBILITY-PRODUCT CALCULATIONS

The solubility-product principle has already been discussed (page 92). In this chapter it will be applied to problems in analytical chemistry. The separation and identification of ions are based very largely upon applications of the solubility-product principle, which, in turn, is based upon experimental studies of the behavior of saturated solutions of slightly soluble electrolytes. For reasons not entirely known, the principle cannot be applied to even moderately soluble electrolytes such as sodium chloride or potassium chlorate. Moreover, it does not hold rigorously for slightly soluble salts in the presence of large amounts of foreign salts. However, for saturated solutions of slightly soluble electrolytes the law holds very satisfactorily, provided the total foreign salt concentration does not exceed 0.3 M.[1]

The following problems will serve to illustrate the various applications of the solubility-product principle in qualitative analysis. In making solubility-product calculations it must be remembered that the concentrations of the ions are expressed in gram-ions [2] per liter. Hence, if the concentration is given in grams or milligrams per liter or some other volume, the first step in a calculation is to compute the concentration in terms of gram-ions per liter. If the electrolyte is completely dissociated, then the concentrations of its ions are obtained directly from the molar solubility of the solute. When the electrolyte is not completely ionized, its molar solubility is multiplied by the percentage ionization expressed as a decimal. Remember that each gram-ion concentration must be raised to the proper power before obtaining the ion-product. Before solving the following problems, the stu-

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[1] Stieglitz, *J. Am. Chem. Soc.*, **30**, 9460 (1908).

[2] Some authors use the term gram-mol, or simply mol, to express the concentration of ions, as well as the concentration of molecules. This is a matter of choice as the numerical values are the same.

dent should review the discussion of the solubility-product principle on pages 92–100.

Case 15. Given the molarity of a slightly soluble electrolyte. Calculate its solubility product constant. Assume complete ionization.

Example 1. The solubility of AgCl is 1.06×10^{-5} mol per liter at 20° C. Calculate the $K_{\text{s.p.}}$ of AgCl.

Silver chloride ionizes as indicated by the ionic equation:

$$AgCl \rightleftharpoons Ag^+ + Cl^-$$

Hence, each mol of AgCl yields 1 gram-ion of Ag^+ ion and 1 gram-ion of Cl^- ion. Therefore in 1 liter of AgCl solution saturated at 20° C., the Ag^+ ion and Cl^- ion concentrations are each 1.06×10^{-5} gram-ion.

The solubility-product equation is

$$C_{Ag^+} \times C_{Cl^-} = K_{\text{s.p.}} \text{ of AgCl}$$

Substituting the gram-ion concentrations in the solubility-product equation,

$$(1.06 \times 10^{-5}) \times (1.06 \times 10^{-5}) = 1.1 \times 10^{-10}$$

$$\therefore \quad K_{\text{s.p.}} \text{ of AgCl} = 1.1 \times 10^{-10}$$

Example 2. The molar solubility of $MgNH_4PO_4$ is 6.3×10^{-5}. Calculate the $K_{\text{s.p.}}$ of $MgNH_4PO_4$.

Magnesium ammonium phosphate ionizes as follows:

$$MgNH_4PO_4 \rightleftharpoons Mg^{++} + NH_4^+ + PO_4^{\equiv}$$

Since 1 mol of $MgNH_4PO_4$ yields, upon complete ionization, 1 gram-ion each of Mg^{++} ion, NH_4^+ ion, and $PO_4^{\equiv}$ ion, the concentration of each of these ions is equal to the molar solubility of the solute. $C_{Mg^{++}} = C_{NH_4^+} = C_{PO_4^{\equiv}} = 6.3 \times 10^{-5}$ gram-ion per liter.

The solubility-product equation is

$$C_{Mg^{++}} \times C_{NH_4^+} \times C_{PO_4^{\equiv}} = K_{\text{s.p.}} \text{ of } MgNH_4PO_4$$

Substituting the gram-ion concentrations for the respective ions, we get

$$(6.3 \times 10^{-5}) \times (6.3 \times 10^{-5}) \times (6.3 \times 10^{-5}) = K_{\text{s.p.}}$$

$$\therefore \quad K_{\text{s.p.}} \text{ of } MgNH_4PO_4 = 2.5 \times 10^{-13}$$

Example 3. The solubility of $Pb_3(PO_4)_2$ in water at 20° C. is 1.7×10^{-7} mol per liter. Calculate its $K_{\text{s.p.}}$

Lead phosphate ionizes according to the equation

$$Pb_3(PO_4)_2 \rightleftharpoons 3Pb^{++} + 2PO_4^{\equiv}$$

Hence, 1 mol of $Pb_3(PO_4)_2$ yields, on complete dissociation, 3 gram-ions of Pb^{++} ion and 2 gram-ions of $PO_4^{\equiv}$ ion.

$$C_{Pb^{++}} = 1.7 \times 10^{-7} \times 3 = 5.1 \times 10^{-7}$$

$$C_{PO_4^{\equiv}} = 1.7 \times 10^{-7} \times 2 = 3.4 \times 10^{-7}$$

The solubility-product equation is

$$C^3_{Pb^{++}} \times C^2_{PO_4^{\equiv}} = K_{s.p.} \text{ of } Pb_3(PO_4)_2$$

Substituting the respective gram-ion concentrations, each raised to the proper power, we get

$$(5.1 \times 10^{-7})^3 \times (3.4 \times 10^{-7})^2 = K_{s.p.}$$
$$\therefore \quad K_{s.p.} \text{ of } Pb_3(PO_4)_2 = 1.5 \times 10^{-32}$$

Case 16. Given the solubility of a slightly soluble electrolyte in terms of grams per unit volume of solution. Calculate its solubility-product constant.

Example. The solubility of Ag_2CrO_4 in water at room temperature is 2.5×10^{-3} g. per 100 ml. Calculate the $K_{s.p.}$ of Ag_2CrO_4. Assume 100 per cent ionization.

$$\text{Mol. wt. } Ag_2CrO_4 = 332$$
$$\frac{2.5 \times 10^{-3} \times 10}{332} = 7.5 \times 10^{-5} \text{ mol per liter}$$

The ionization of Ag_2CrO_4 is expressed by the following equation:

$$Ag_2CrO_4 \rightleftharpoons 2Ag^+ + CrO_4^{=}$$

Hence, each mol of Ag_2CrO_4 yields, on complete ionization, 2 gram-ions of Ag^+ ion and 1 gram-ion of $CrO_4^{=}$ ion.

$$C_{Ag^+} = 7.5 \times 10^{-5} \times 2 = 1.5 \times 10^{-4} \text{ gram-ion per liter}$$
$$C_{CrO_4^{=}} = 7.5 \times 10^{-5} \text{ gram-ion per liter.}$$

The solubility-product equation is

$$C^2_{Ag^+} \times C_{CrO_4^{=}} = K_{s.p.}$$

Substituting the gram-ion concentrations in the solubility-product equation and raising each to the proper power, we have

$$(1.5 \times 10^{-4})^2 \times (7.5 \times 10^{-5}) = K_{s.p.}$$
$$\therefore \quad K_{s.p.} \text{ of } Ag_2CrO_4 = 1.7 \times 10^{-12}$$

Case 17. Given the solubility of a slightly soluble electrolyte which is not completely ionized. Calculate its $K_{s.p.}$

Example. The solubility of $AgC_2H_3O_2$ in water at 16° C. is 0.060 mol per liter. Conductivity measurements indicate the salt is 71 per cent ionized in its saturated solution at 16° C. Calculate its $K_{s.p.}$

The ionization is expressed as follows:

$$AgC_2H_3O_2 \rightleftharpoons Ag^+ + C_2H_3O_2^-$$

$$C_{Ag^+} = 0.060 \times 0.71 = 0.0426 \text{ gram-ion per liter}$$
$$C_{C_2H_3O_2^-} = 0.060 \times 0.71 = 0.0426 \text{ gram-ion per liter}$$

Substituting in the solubility-product equation,

$$0.0426 \times 0.0426 = K_{\text{s.p.}}$$
$$\therefore \quad K_{\text{s.p.}} \text{ of } AgC_2H_3O_2 = 1.8 \times 10^{-3}$$

Case 18. Given the concentration of one of the ions in a saturated solution of a slightly soluble electrolyte. Calculate the $K_{\text{s.p.}}$

Example. The concentration of Ag^+ ion in a saturated Ag_3PO_4 solution is 4.8×10^{-5} gram-ion per liter. What is the $K_{\text{s.p.}}$ of Ag_3PO_4? Assume 100 per cent ionization.

Ag_3PO_4 ionizes as follows:

$$Ag_3PO_4 \rightleftharpoons 3Ag^+ + PO_4^{\equiv}$$

Hence 3 gram-ions of Ag^+ ion are equivalent to 1 gram-ion of $PO_4^{\equiv}$ ion and 1 gram-mol of Ag_3PO_4. Therefore the saturated solution is $\frac{4.8 \times 10^{-5}}{3} = 1.6 \times 10^{-5}$ molar with respect to Ag_3PO_4 and contains 1.6×10^{-5} gram-ion of $PO_4^{\equiv}$ per liter.

Substituting the gram-ion concentrations in the solubility-product equation and raising each to its proper power, we obtain

$$(4.8 \times 10^{-5})^3 \times (1.6 \times 10^{-5}) = K_{\text{s.p.}}$$
$$\therefore \quad K_{\text{s.p.}} \text{ of } Ag_3PO_4 = 1.8 \times 10^{-18}$$

Case 19. Given the solubility-product constant of a compound which is completely ionized in its saturated solution. Calculate the solubility of the compound.

Example 1. The $K_{\text{s.p.}}$ of AgI is 1.5×10^{-16}. What is the solubility of AgI (*a*) in mols per liter and (*b*) in grams per liter?

AgI ionizes as follows:

$$AgI \rightleftharpoons Ag^+ + I^-$$

Since 1.22×10^{-8} is the gram-ion concentration of both Ag^+ ion and I^- ion, it is also the molar solubility of AgI. To convert molar solubility into grams per liter, multiply by the molecular weight.

Hence, $1.22 \times 10^{-8} \times 234.8 = 2.86 \times 10^{-6}$ g. per liter.

✓ **Example 2.** The $K_{\text{s.p.}}$ of $Mg(OH)_2$ is 3.4×10^{-11} at 25° C. Calculate the molar solubility of $Mg(OH)_2$.

$Mg(OH)_2$ dissociates according to the equation

$$Mg(OH)_2 \rightleftharpoons Mg^{++} + 2OH^-$$

Since concentration $(OH^-) = 2(Mg^{++})$, we can state the solubility product as

$$Mg^{++} \times [2(Mg^{++})]^2 = 4(Mg^{++})^3 = K_{S.P.}$$
$$4(Mg^{++})^3 = 3.4 \times 10^{-11}$$
$$Mg^{++} = \sqrt[3]{\frac{3.4 \times 10^{-11}}{4}}$$
$$= \sqrt[3]{8.5 \times 10^{-12}}$$
$$= 2.0 \times 10^{-4} \text{ gram-ion per liter}$$

Since each gram-ion of Mg^{++} represents 1 mol of $Mg(OH)_2$, it follows that the solubility of $Mg(OH)_2$ is 2.0×10^{-4} mol per liter.

We may solve the above problem in a slightly different manner.

Let

$$x = C_{Mg^{++}}; \quad 2x = C_{OH^-}$$
$$x \times (2x)^2 = K_{S.P.} = 3.4 \times 10^{-11}$$
$$4x^3 = 3.4 \times 10^{-11}$$
$$= \sqrt{\frac{3.4 \times 10^{-11}}{4}}$$
$$= 2.0 \times 10^{-4} \text{ gram-ion per liter}$$
$$\therefore \quad \text{Solubility of } Mg(OH)_2 \text{ is } 2.0 \times 10^{-4} \text{ mol per liter}$$

Case 20. Given the solubility-product constant of a compound which is not completely ionized. Calculate its solubility. This is the reverse of *Case 17.*

Example. The $K_{S.P.}$ of $AgC_2H_3O_2$ is 1.8×10^{-3} at 16° C., and the salt is 71 per cent ionized. Calculate its solubility.

Let x = molar solubility. If ionization were 100 per cent, then $C_{Ag^+} = x$ and $C_{C_2H_3O_2^-} = x$. But the salt is only 71 per cent ionized. Hence $C_{Ag^+} =$ 0.71 and $C_{C_2H_3O_2^-} = 0.71$

Substituting in the solubility-product equation

$$0.71x \times 0.71x = 1.8 \times 10^{-3}$$
$$0.50x^2 = 1.8 \times 10^{-3}$$
$$x^2 = \frac{1.8 \times 10^{-3}}{0.50}$$
$$x^2 = 3.6 \times 10^{-3} = 36 \times 10^{-4}$$
$$x = 6 \times 10^{-2} \text{ mol per liter}$$

The molecular weight of $AgC_2H_3O_2 = 167$. Therefore, $0.06 \times 167 = 10.0$ g. per liter.

PROBLEMS[3]

1. The solubility of AgCl in water at 20° C. is 0.0015 g. per liter. What is its solubility in mols per liter?

Ans. 1.05×10^{-5} mol per l.

2. From the data in problem 1, calculate the solubility-product constant $K_{s.p.}$, for AgCl.

Ans. 1.1×10^{-10}.

3. The solubility of $BaSO_4$ at 15°, 20°, and 100° C. is 0.00021, 0.00024, and 0.00039 gram per 100 ml., respectively. Calculate its molar solubility at these temperatures.

Ans. 9×10^{-6} mol per l.
1×10^{-5} mol per l.
1.7×10^{-5} mol per l.

4. Calculate the $K_{s.p.}$ value for $BaSO_4$ at 15°, 20°, and 100° C., respectively, using the data in problem 3. In general, what may be said regarding the effect of temperature upon the solubility-product constant?

Ans. 8.1×10^{-11}.
1.0×10^{-10}.
2.9×10^{-10}.

5. Compare the $K_{s.p.}$ of CaC_2O_4 at 13° C. with its value at 95° C. The solubility of CaC_2O_4 in water at 13° C. is 0.0067 g. per liter. At 95° C. the solubility is 0.014 g. per liter.

Ans. 2.7×10^{-9}, 1.2×10^{-8}.

6. The solubility of $PbCrO_4$ in water at room temperature is 4.3×10^{-6} g. per 100 ml. Calculate the $K_{s.p.}$ of $PbCrO_4$.

Ans. 1.8×10^{-14}.

7. The solubility of $PbCl_2$ in water at room temperature is about 10 g. per liter. Calculate the (approximate) $K_{s.p.}$ of $PbCl_2$.

Ans. 1.9×10^{-4}.

8. What is the solubility-product constant of Ag_2CrO_4, if the solubility of the salt in water at room temperature is 2.5×10^{-3} g. per 100 ml.?

Ans. 1.7×10^{-12}.

9. The solubility of Hg_2Cl_2 in water at room temperature is 3.8×10^{-5} g. per 100 ml. Calculate the $K_{s.p.}$ of Hg_2Cl_2. Express the equilibrium as follows: $Hg_2Cl_{2(solid)} \rightleftharpoons Hg_2^{++} + 2Cl^-$.

Ans. 2.1×10^{-18}.

10. Calculate the $K_{s.p.}$ of Ag_3AsO_4, its solubility in water at 20° C. being 8.5×10^{-4} g. per 100 ml.

Ans. 3.1×10^{-18}.

11. What is the $K_{s.p.}$ of $Ca_3(PO_4)_2$? The solubility of $Ca_3(PO_4)_2$ in water at room temperature is 2×10^{-3} g. per 100 ml.

Ans. 1.2×10^{-19}.

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[3] Unless otherwise stated, assume complete ionization in making the calculations involving the solubility product.

12. Calculate the $K_{\text{s.p.}}$ of $MgNH_4PO_4$. The solubility of this compound in water at room temperature is 8.6×10^{-3} g. per liter.

Ans. 2.5×10^{-13}.

13. The solubility of CdS is 2×10^{-14} mol per liter. What is its $K_{\text{s.p.}}$?

Ans. 4×10^{-28}.

14. Compare the $K_{\text{s.p.}}$ of the silver halides. Their molar solubilities per liter in water at room temperature are as follows: AgCl, 1.06×10^{-5}; AgBr, 5.9×10^{-7}; AgI, 1.3×10^{-8}.

Ans. (*a*) 1.1×10^{-10}.
(*b*) 3.5×10^{-13}.
(*c*) 1.7×10^{-16}.

15. Calculate the $K_{\text{s.p.}}$ of the following sulfides, their solubilities in mols per liter being as follows: (*a*) CuS, 5×10^{-21}; (*b*) HgS, 1.8×10^{-27}; (*c*) SnS, 1×10^{-13}; (*d*) FeS, 6×10^{-10}; (*e*) NiS, 1.2×10^{-12}.

Ans. (*a*) 2.5×10^{-41}. (*d*) 3.6×10^{-19}.
(*b*) 3.2×10^{-54}. (*e*) 1.4×10^{-24}.
(*c*) 1×10^{-26}.

16. Calculate the $K_{\text{s.p.}}$ of the following hydroxides, their solubilities in mols per liter being as follows: (*a*) $Zn(OH)_2$, 6.3×10^{-7}; (*b*) $Mg(OH)_2$, 2.0×10^{-4}; (*c*) $Fe(OH)_2$, 1.6×10^{-5}; (*d*) $Fe(OH)_3$, 4.5×10^{-10}.

Ans. (*a*) 1.0×10^{-18}. (*c*) 1.6×10^{-14}.
(*b*) 3.4×10^{-11}. (*d*) 1.1×10^{-36}.

17. Calculate the solubilities of the following compounds, being given their solubility-product constants at room temperature: (*a*) $K_{\text{s.p.}}$ of $CaCO_3$, 1.2×10^{-8}; (*b*) $K_{\text{s.p.}}$ of $SrCO_3$, 1.6×10^{-9}; (*c*) $K_{\text{s.p.}}$ of $BaCO_3$, 8.1×10^{-9}. Report the solubilities both in terms of mols per liter and grams per liter.

Ans. (*a*) 1.1×10^{-4} mol per l., 1.1×10^{-2} g. per l.
(*b*) 4×10^{-5} mol per l., 5.9×10^{-3} g. per l.
(*c*) 9×10^{-5} mol per l., 1.8×10^{-2} g. per l.

18. From the values of $K_{\text{s.p.}}$, calculate the solubilities (mols per liter) of the following salts: (*a*) BaF_2, $K_{\text{s.p.}} = 1.7 \times 10^{-6}$; (*b*) $PbBr_2$, $K_{\text{s.p.}} = 7.9 \times 10^{-5}$; (*c*) Ag_2SO_4, $K_{\text{s.p.}} = 7.0 \times 10^{-5}$.

Ans. (*a*) 7.5×10^{-3} mol per l.
(*b*) 2.7×10^{-2} mol per l.
(*c*) 2.6×10^{-2} mol per l.

19. How many milligrams of each of the following compounds are present in a liter of its saturated aqueous solution: (*a*) $K_{\text{s.p.}}$ of Hg_2I_2, 1.2×10^{-28}; (*b*) $K_{\text{s.p.}}$ of $MgNH_4PO_4$, 2.5×10^{-13}; (*c*) $K_{\text{s.p.}}$ of Ag_3PO_4, 1.8×10^{-18}?

Ans. (*a*) 2.0×10^{-4} mg.
(*b*) 8.7 mg.
(*c*) 6.7 mg.

20. Calculate the solubilities (grams per liter) of the following salts, being given their $K_{\text{s.p.}}$ values: (*a*) $Ag_2Cr_2O_7$, $K_{\text{s.p.}} = 2 \times 10^{-7}$; (*b*) K_2PtCl_6, $K_{\text{s.p.}} = 4.9 \times 10^{-5}$; (*c*) $Pb_3(PO_4)_2$, $K_{\text{s.p.}} = 1.5 \times 10^{-32}$.

Ans. (*a*) 1.6 g. per l.
(*b*) 11 g. per l.
(*c*) 1.4×10^{-4} g. per l.

21. The $K_{s.p.}$ of CaC_2O_4 is 2.6×10^{-9}. How many milligrams of Ca^{++} ion and of $C_2O_4^{=}$ ion are present in 10 ml. of a saturated CaC_2O_4 solution?

Ans. 2.0×10^{-2} mg. Ca^{++}.
4.5×10^{-2} mg. $C_2O_4^{=}$.

22. Calculate the Zn^{++} and OH^{-} ion concentrations in a liter of saturated $Zn(OH)_2$ solution, the $K_{s.p.}$ of $Zn(OH)_2$ being 1.0×10^{-18}.

Ans. 4.1×10^{-5} g. per l.
4.3×10^{-5} g. per l.

23. Calculate from $K_{s.p.}$ values the $PO_4^{\equiv}$ ion concentration in a liter of the following saturated solutions: (*a*) $MgNH_4PO_4$, $K_{s.p.} = 2.5 \times 10^{-13}$; (*b*) Ag_3PO_4, $K_{s.p.} = 1.8 \times 10^{-18}$; (*c*) $Pb_3(PO_4)_2$, $K_{s.p.} = 1.5 \times 10^{-32}$.

Ans. (*a*) 6.0×10^{-3} g. per l.
(*b*) 1.5×10^{-3} g. per l.
(*c*) 3.2×10^{-5} g. per l.

24. Compare the solubilities of the alkaline earth sulfates, being given their $K_{s.p.}$ values: (*a*) $K_{s.p.}$ of $CaSO_4 = 6.1 \times 10^{-5}$; (*b*) $K_{s.p.}$ of $SrSO_4 = 2.8 \times 10^{-7}$; (*c*) $K_{s.p.}$ of $BaSO_4 = 1.2 \times 10^{-10}$.

Ans. (*a*) 7.8×10^{-3} gram-mol per l.
(*b*) 5.3×10^{-4} gram-mol per l.
(*c*) 1.1×10^{-5} gram-mol per l.

25. Given the $K_{s.p.}$ of each of the following compounds, compare their solubilities: (*a*) CuS, $K_{s.p.} = 2.5 \times 10^{-41}$; (*b*) Cu_2S, $K_{s.p.} = 2 \times 10^{-47}$; (*c*) Tl_2S, $K_{s.p.} = 7.0 \times 10^{-23}$; (*d*) $Fe(OH)_2$, $K_{s.p.} = 1.6 \times 10^{-14}$; (*b*) $Fe(OH)_3$, $K_{s.p.} = 1.1 \times 10^{-36}$.

Ans. (*a*) 5×10^{-21}. (*d*) 1.6×10^{-5}.
(*b*) 1.7×10^{-16}. (*e*) 4.5×10^{-10}.
(*c*) 2.6×10^{-8}.

26. When is it possible to obtain a comparison of the relative solubilities of two or more compounds by a direct comparison of their respective solubility-product constants?

SOME APPLICATIONS OF THE SOLUBILITY-PRODUCT PRINCIPLE TO PRECIPITATION

Before solving examples of this type let us summarize briefly the applications of the solubility-product principle:

1. Before precipitation of a slightly soluble electrolyte can take place, the product of its ion concentrations must exceed the $K_{s.p.}$ (at the given temperature).

2. When the ion concentration product just equals the $K_{s.p.}$, the solution is saturated.

3. When the ion concentration product exceeds the $K_{s.p.}$, precipitation will take place **provided sufficient time is allowed for the precipitate to form.** Note that the solubility-product principle

makes no mention of the time factor. Many precipitates form very slowly, especially at the low concentrations often dealt with in qualitative and quantitative analyses (see page 101).

4. Conversely to 1, in order to dissolve a precipitate, the product of the ion concentrations must be kept below the $K_{s.p.}$ of the precipitate (see page 158).

5. It follows from 4 that, in order to prevent precipitation of a slightly soluble electrolyte, a reagent must be present which will maintain the concentration of one of the ions so low that the $K_{s.p.}$ cannot be reached.

Case 21. Given the concentration of one of the ions of a slightly soluble electrolyte and its $K_{s.p.}$ Calculate the concentration which the other ion must attain before a precipitate can form.

Example 1. A test solution of a barium salt contains 10 mg. of Ba^{++} ion per ml., and the $K_{s.p.}$ of $BaCO_3$ is 8.1×10^{-9}. Calculate the concentration of $CO_3^{=}$ ion which must be exceeded before $BaCO_3$ can precipitate.

First, convert milligrams per milliliter to gram-ions per liter.

$$\begin{aligned} \text{At. wt. Ba} &= 137.36 \text{ or } 137 \text{ (approximately)} \\ 10 \text{ mg. } Ba^{++} \text{ per ml.} &= 10{,}000 \text{ mg. per liter} \\ &= 10 \text{ g. per liter} \\ \therefore \quad \tfrac{10}{137} \text{ gram-ion } Ba^{++} \text{ per liter} &= 0.073 \text{ gram-ion per liter} \end{aligned}$$

Substituting in the solubility-product equation for $BaCO_3$,

$$\begin{aligned} 0.073 \times C_{CO_3^{=}} &= 8.1 \times 10^{-9} \\ C_{CO_3^{=}} &= \frac{8.1 \times 10^{-9}}{0.073} \\ &= 11.1 \times 10^{-8} = 1.1 \times 10^{-7} \end{aligned}$$

Hence a $CO_3^{=}$ concentration of 1.1×10^{-7} gram-ion per liter must be exceeded before $BaCO_3$ can precipitate. To convert this into grams per liter multiply by the molecular weight of $CO_3^{=}$, which is 60.

$$1.1 \times 10^{-7} \times 60 = 66 \times 10^{-7} = 6.6 \times 10^{-6} \text{ g. per liter}$$

Note that the concentrations of Ba^{++} ion and $CO_3^{=}$ ion are not equal. It is only in a saturated pure water solution of $BaCO_3$ that the Ba^{++} and $CO_3^{=}$ ions are in equal concentration. To check our calculation, substitute the gram-ion concentrations of Ba^{++} and $CO_3^{=}$ in the solubility-product equation and solve for $K_{s.p.}$

$$0.073 \times 1.1 \times 10^{-7} = K_{s.p.} \text{ of } BaCO_3$$

$K_{s.p.}$ of $BaCO_3 = 8.1 \times 10^{-9}$, which is in agreement with the value of $K_{s.p.}$ given in the example. This is the first time the suggestion has been made to check a calculation. The student will do well to get into the habit of checking his calculations by reversing his computations when the process is not too involved.

Example 2. What OH^- ion concentration must be just exceeded before $Fe(OH)_3$ can precipitate from a 0.1 *M* $FeCl_3$ solution which is 65 per cent ionized? $K_{s.p.}$ of $Fe(OH)_3 = 1.1 \times 10^{-36}$.

The ionization of $Fe(OH)^3$ is expressed as follows:

$$Fe(OH)_3 \rightleftharpoons Fe^{+++} + 3OH^-$$

Hence in a saturated pure aqueous solution of $Fe(OH)_3$, $C_{Fe^{+++}} = \frac{1}{3}C_{OH^-}$ or $C_{OH^-} = 3C_{Fe^{+++}}$. In the 0.1 *M* $FeCl_3$ solution to which OH^- ions are to be added:

Let $x = C_{OH^-}$ which must be exceeded before $Fe(OH)_3$ can precipitate.

Obviously $\frac{1}{3}x$ is not the concentration of Fe^{+++} in the solution. This is $0.1 \times 0.65 = 0.065$ mol per liter.

Substituting in the solubility-product equation,

$$0.065 \times x^3 = 1.1 \times 10^{-36}$$

$$x^3 = \frac{1.1 \times 10^{-36}}{0.065} = 17 \times 10^{-36}$$

$$x = \sqrt[3]{17 \times 10^{-36}} = 2.6 \times 10^{-12} \text{ gram-ion per liter}$$

Example 3. How many milligrams of CrO_4^- ion must be added to 10 ml. of a solution containing 0.01 mg. of Pb^{++} ion, in order to start precipitation of $PbCrO_4$? $K_{s.p.}$ of $PbCrO_4 = 1.8 \times 10^{-14}$.

10 ml. contain 0.01 mg. Pb^{++}
1000 ml. contain 1.0 mg. Pb^{++}
1000 ml. contain 0.001 g. Pb^{++}
At. wt. Pb = 207 (approximately)

$$\therefore \quad \frac{0.001}{207} = 4.8 \times 10^{-6} \text{ gram-ion } Pb^{++} \text{ per liter}$$

Substituting in the $K_{s.p.}$ equation for $PbCrO_4$,

$$4.8 \times 10^{-6} \times C_{CrO_4^-} = 1.8 \times 10^{-14}$$

$$C_{CrO_4^-} = \frac{1.8 \times 10^{-14}}{0.48 \times 10^{-5}}$$

$$= 3.8 \times 10^{-9} \text{ gram-ion per liter}$$

To convert into grams per liter, multiply by the molecular weight of CrO_4^- ion which is 116 (approximately).

$$3.8 \times 10^{-9} \times 116 = 4.4 \times 10^{-7} \text{ g. per liter}$$

$$= 4.4 \times 10^{-4} \text{ mg. per liter}$$

$\therefore$ A little more than 4.4×10^{-6} mg. CrO_4^- ion must be added to 10 ml. of the Pb^{++} ion solution in order to start precipitation of $PbCrO_4$.

Example 4. How many milligrams of NH_4Cl are required to just start precipitation of AgCl in 10 ml. of a solution containing 1 mg. of Ag^+ ion? $K_{s.p.}$ of AgCl $= 1.1 \times 10^{-10}$. Assume the NH_4Cl to be 100 per cent ionized.

10 ml. contain 1 mg. Ag^+ ion
1000 ml. contain 100 mg. Ag^+ ion
1000 ml. contain 0.1 g. Ag^+ ion
At. wt. Ag = 108 (approximately)

$$\frac{0.1}{108} = 0.00093$$
$$= 9.3 \times 10^{-4} \text{ gram-ion } Ag^+ \text{ ion}$$

Substituting in the solubility-product equation of AgCl, we have

$$9.3 \times 10^{-4} \times C_{Cl^-} = 1.1 \times 10^{-10}$$
$$C_{Cl^-} = \frac{1.1 \times 10^{-10}}{9.3 \times 10^{-4}}$$
$$= 1.2 \times 10^{-7} \text{ gram-ion } Cl^- \text{ per liter}$$

To convert into grams per liter, multiply by the atomic weight of chlorine:

$$1.2 \times 10^{-7} \times 35.5 = 4.3 \times 10^{-6} \text{ g. } Cl^- \text{ per liter}$$

Calculating the Cl^- to its equivalent of NH_4Cl,

$$4.3 \times 10^{-6} \times \frac{53.5}{35.5} = 6.5 \times 10^{-6} \text{ g. } NH_4Cl \text{ per liter}$$
$$= 6.5 \times 10^{-3} \text{ mg. } NH_4Cl \text{ per liter}$$

∴ A little more than 6.5×10^{-5} mg. of NH_4Cl must be added to 10 ml. of the Ag^+ ion solution in order to start precipitation of AgCl.

Example 5. If 5 ml. of solution containing 4×10^{-4} gram-ion of Sr^{++} ion per liter is mixed with 5 ml. of solution containing 4×10^{-4} gram-ion of $C_2O_4^{=}$ ion per liter, will SrC_2O_4 precipitate? $K_{s.p.}$ of SrC_2O_4 is 5.6×10^{-8}.

Note that upon mixing the two solutions the concentration of both the Sr^{++} and $C_2O_4^{=}$ ions is reduced to one-half the original concentration; i.e., the concentration of each ion after mixing equal volumes is 2×10^{-4} gram-ion per liter. Substituting the latter concentration in the solubility-product equation of SrC_2O_4,

$$(2 \times 10^{-4}) \times (2 \times 10^{-4}) = 4 \times 10^{-8}$$

Since the value of the ion concentration product (4×10^{-8}) is less than that of the $K_{s.p.}$ of SrC_2O_4 (5.6×10^{-8}), precipitation cannot take place.

Example 6. Suppose that in example 5 the $C_2O_4^{=}$ ion solution had contained 8×10^{-4} gram-ion per liter. Would SrC_2O_4 precipitate on mixing two 5-ml. portions of the solutions?

After mixing, the Sr^{++} ion concentration will be 2×10^{-4} gram-ion per liter and the $C_2O_4^{=}$ ion concentration will be 4×10^{-4} gram-ion per liter. Substituting in the solubility-product equation for SrC_2O_4, we get

$$(2 \times 10^{-4}) \times (4 \times 10^{-4}) = 8 \times 10^{-8}$$

Therefore, SrC_2O_4 should precipitate; the ion concentration product (8×10^{-8}) being greater than the $K_{s.p.}$ for SrC_2O_4. In other words, immediately upon mixing the two solutions, the resulting solution is supersaturated with respect to SrC_2O_4. In order to attain equilibrium, some solid SrC_2O_4 must separate out of solution.

Example 7. In example 6, how much SrC_2O_4 must precipitate in order for the 10 ml. solution to reach equilibrium, or to become saturated?

Let x equal the amount by which the concentration of each ion must be reduced in order for their product to equal the solubility product. Then

$$(2 \times 10^{-4} - x)(4 \times 10^{-4} - x) = 5.6 \times 10^{-8}$$
$$(8 \times 10^{-8}) - (6 \times 10^{-4})x + x^2 = 5.6 \times 10^{-8}$$
$$x^2 - (6 \times 10^{-4})x + (2.4 \times 10^{-8}) = 0$$

Applying the quadratic formula:

$$x = \frac{6 \times 10^{-4} \pm \sqrt{(36 \times 10^{-8}) - (9.6 \times 10^{-8})}}{2}$$
$$= \frac{6 \times 10^{-4} \pm \sqrt{26.4 \times 10^{-8}}}{2}$$
$$= 3 \times 10^{-4} \pm 2.57 \times 10^{-4}$$

$= 0.43 \times 10^{-4}$ gram-ion per liter, the other mathematically possible value being excluded because it would leave negative ionic concentrations when subtracted from the original values.

Since the concentration of each ion is reduced by this value, the same number of mols of SrC_2O_4 would have to precipitate out of 1 liter of the supersaturated solution in order to restore equilibrium. Since only 10 ml. of the solution was actually used, the amount of SrC_2O_4 precipitated would be 4.3×10^{-7} mol. Multiplying by the molecular weight of SrC_2O_4 (176 approximately) we obtain the gram quantity:

$$4.3 \times 10^{-7} \times 176 = 7.6 \times 10^{-5} \text{ g. of } SrC_2O_4$$

The above examples illustrate the important function of the concentration in precipitation reactions. The same **quantities** of two different ions may be present in two sets of solutions, and yet, upon mixing the solutions of one set a precipitate may be obtained, while upon mixing the other set no precipitate may appear. In order to obtain a precipitate with the latter set (without adding any more ions to either solution), it will be necessary to concentrate either by evaporating one or both solutions before mixing, or by evaporating the mixed solution.

PROBLEMS

1. What gram-ion concentration of Cl^- ion is required to form sufficient AgCl to saturate a liter of solution containing 0.005 gram-ion of Ag^+? $K_{\text{s.p.}}$ of AgCl $= 1.1 \times 10^{-10}$.

Ans. 2.2×10^{-8} gram-ion per l.

2. Calculate the gram-ion quantity of OH^- ion that must be added to 100 ml. of a solution containing 10 mg. of Fe^{+++} ion in order to just exceed the saturation point of $Fe(OH)_3$. $K_{\text{s.p.}}$ of $Fe(OH)_3 = 1.1 \times 10^{-36}$.

Ans. 8.5×10^{-13} gram-ion.

3. If 10 ml. of solution contain 25 mg. of Pb^{++} ion, how many milligrams of Cl^- ion must be added to just start precipitation of $PbCl_2$? $K_{\text{s.p.}}$ of $PbCl_2 = 2.4 \times 10^{-4}$.

Ans. 50 mg.

4. Suppose that 0.01 mol of $SO_4^{=}$ ion is added to 100 ml. of a solution which contains 8.5×10^{-7} gram-ion of Ba^{++} ion. Should $BaSO_4$ precipitate? $K_{\text{s.p.}}$ of $BaSO_4 = 1.2 \times 10^{-10}$.

Ans. Yes.

5. How many milliliters of a 1 *M* solution of $(NH_4)_2C_2O_4$ must be added to 50 ml. of a 0.05 *M* $Ca(NO_3)_2$ solution to just start precipitation of CaC_2O_4? $K_{\text{s.p.}}$ of $CaC_2O_4 = 2.6 \times 10^{-9}$.

Ans. 2.6×10^{-6} ml.

6. (*a*) A certain solution contains 10 mg. of Ag^+ ion per milliliter. How many milligrams of $PO_4^{\equiv}$ ion must be added to 10 ml. of the solution to just start precipitation of Ag_3PO_4? (*b*) How many milligrams of $PO_4^{\equiv}$ would be required to complete the precipitation? $K_{\text{s.p.}}$ for $Ag_3PO_4 = 1.8 \times 10^{-18}$.

Ans. (*a*) 7.9×10^{-14} mg.
(*b*) 29.3 mg.

7. (*a*) Suppose 5 mg. of Br^- ion to be added to 100 ml. of a solution which contains 0.1 mg. of Hg_2^{++} ion. Will Hg_2Br_2 precipitate? (*b*) How many milligrams of Br^- ion will be required to completely precipitate the mercury as Hg_2Br_2? $K_{\text{s.p.}}$ of $Hg_2Br_2 = 1.3 \times 10^{-21}$.

Ans. (*a*) Yes.
(*b*) 0.04 mg.

8. How much chloroplatinate ion, $[PtCl_6]^{=}$, must be added to just saturate with K_2PtCl_6, 50 ml. of a solution which contains 10 mg. of K^+ ion? $K_{\text{s.p.}}$ of $K_2PtCl_6 = 4.9 \times 10^{-5}$.

Ans. 9.6 g.

9. To 100 ml. of a 0.001 *M* $AgNO_3$ solution is added 1 ml. of a 0.001 *M* $SO_4^{=}$ solution. Will Ag_2SO_4 precipitate? (Disregard the slight increase in the volume of the $AgNO_3$ solution.) $K_{\text{s.p.}}$ of $Ag_2SO_4 = 7.0 \times 10^{-5}$.

Ans. No.

10. Calculate the milligrams of $(NH_4)_2CO_3$ which must be added to just start precipitation of $SrCO_3$ in 50 ml. of a solution containing 10 mg. of Sr^{++} ion. $K_{\text{s.p.}}$ of $SrCO_3 = 1.6 \times 10^{-9}$.

Ans. 3.4×10^{-3} mg.

11. How many milligrams of NH_4Cl must be added to obtain a precipitate of TlCl in 10 ml. of a solution containing 0.1 mg. of Tl^+ ion? $K_{\text{s.p.}}$ of $TlCl = 2.0 \times 10^{-4}$.

Ans. 2180 mg.

12. A liter of H_2S solution saturated at 25° C. contains 1.2×10^{-15} gram-ion of $S^=$ ion. What quantity (milligrams) of each of the following ions must be present in 100 ml. to just saturate the solution with the corresponding sulfide: (*a*) Hg^{++}, (*b*) Pb^{++}, (*c*) Bi^{+++}, (*d*) Cu^{++}, and (*e*) Cd^{++}? See page 98 for solubility-product values.

Ans. (*a*) 5.0×10^{-35} mg. (*d*) 1.3×10^{-22} mg.
(*b*) 5.8×10^{-9} mg. (*e*) 3.6×10^{-9} mg.
(*c*) 6.5×10^{-10} mg.

13. To 10 ml. of a solution containing 5 mg. of Pb^{++} ion are added 10 ml. of a 1 *M* NH_4Cl solution. (*a*) Will a precipitate of $PbCl_2$ form? (*b*) How many milligrams of Pb^{++} ion must be present to just saturate the solution with $PbCl_2$? $K_{\text{s.p.}}$ of $PbCl_2 = 2.4 \times 10^{-4}$.

Ans. (*a*) Yes.
(*b*) 4.0 mg.

14. Ten grams of Na_2CrO_4 are added to 100 ml. of a saturated $BaCrO_4$ solution. What is the concentration of Ba^{++} ion after equilibrium is reached? $K_{\text{s.p.}}$ of $BaCrO_4 = 2.3 \times 10^{-10}$.

Ans. 3.7×10^{-10} gram-ion per l.

15. Ten grams of $MgCl_2$ and 20 g. of NH_4Cl are added to 100 ml. of a saturated $MgNH_4PO_4$ solution. Calculate the $PO_4^{\equiv}$ ion concentration that will be present when the solution is in equilibrium. $K_{\text{s.p.}}$ of $MgNH_4PO_4 = 2.5 \times 10^{-13}$.

Ans. 6.4×10^{-14} gram-ion per l.

Case 22. Precipitations involving an ionization constant as well as a solubility-product constant.

Important applications of *Case 22* in qualitative analysis are the precipitation of the copper and tin group sulfides with H_2S and the precipitation of the trivalent metals of the iron and aluminum groups by means of NH_4OH.

Example 1. What quantity of Cd^{++} ion remains unprecipitated when 100 ml. of a 0.3 *M* HNO_3 solution containing Cd^{++} ions are saturated with H_2S at room temperature? $K_{\text{s.p.}}$ of $CdS = 3.8 \times 10^{-29}$; $C^2_{H^+} \times C_{S^=} = 1.1 \times 10^{-23}$; 0.3 *M* HNO_3 is 90 per cent ionized.

According to the solubility-product principle, the amount of Cd^{++} ion remaining unprecipitated will depend upon the $S^=$ ion concentration, which in turn will depend upon the H^+ ion concentration of the solution. To precipitate CdS, its $K_{\text{s.p.}}$ must be

$$C_{\text{Cd}^{++}} \times C_{\text{S}^{=}} = 3.8 \times 10^{-28}$$

On page 134 the $S^{=}$ ion concentration in a 0.3 M HNO_3 solution saturated with H_2S at room temperature and under atmospheric pressure was calculated to be 1.5×10^{-22} gram-ion per liter. Substituting this value in the above $K_{\text{s.p.}}$ equation, we obtain

$$C_{\text{Cd}^{++}} = \frac{3.8 \times 10^{-28}}{1.5 \times 10^{-22}} = 2.5 \times 10^{-6} \text{ gram-ion per liter}$$

$$\text{At. wt. Cd} = 112.4$$

Hence,

$$C_{\text{Cd}^{++}} = 2.5 \times 10^{-6} \times 112.4 = 2.8 \times 10^{-4} \text{ g. per liter}$$

or 2.8×10^{-4} mg. per ml.

Therefore only 0.028 mg. (approximately 0.03 mg.) of Cd^{++} remains unprecipitated upon saturating with H_2S, 100 ml. of a 0.3 M HNO_3 solution of Cd^{++} ions.

A second method of calculating the amount of Cd^{++} remaining unprecipitated is as follows: The precipitation of CdS is controlled simultaneously by two equilibria: (1) the equilibrium between Cd^{++} ions and $S^{=}$ ions, and (2) the equilibrium between H^+ ions and $S^{=}$ ions. These relationships are expressed by the following equations:

$$C_{\text{Cd}^{++}} \times C_{\text{S}^{=}} = 3.8 \times 10^{-28} \quad (1)$$

$$C^2_{\text{H}^+} \times C_{\text{S}^{=}} = 1.1 \times 10^{-23} \quad (2)$$

Dividing (1) by (2) we get

$$\frac{C_{\text{Cd}^{++}}}{C^2_{\text{H}^+}} = \frac{3.8 \times 10^{-28}}{1.1 \times 10^{-23}}$$

$$C_{\text{Cd}^{++}} = \frac{3.8 \times 10^{-28}}{1.1 \times 10^{-23}} \times C^2_{\text{H}^+} \quad (3)$$

Hence, the concentration of Cd^{++} remaining in the solution is directly proportional to the square of the H^+ ion concentration. In 0.3 M HNO_3 which is 90 per cent ionized,

$$C_{\text{H}^+} = 0.3 \times 0.90 = 0.27 \text{ mol per liter}$$

Substituting this value in equation (3),

$$\begin{aligned} C_{\text{Cd}^{++}} &= \frac{3.8 \times 10^{-28}}{1.1 \times 10^{-23}} \times (0.27)^2 \\ &= 3.45 \times 10^{-5} \times 0.073 \\ &= 2.5 \times 10^{-6} \text{ gram-ion per liter} \end{aligned}$$

Converting to gram concentration, we get

$$2.5 \times 10^{-6} \times 112.4 = 2.8 \times 10^{-4} \text{ g. per liter}$$

It should be pointed out that equation (1) varies with the valence of the metal being precipitated and hence the form of equation (3) will also vary. For example, the solubility-product equation of Bi_2S_3 is:

$$C^2_{Bi^{+++}} \times C^3_{S^{=}} = K_{(Bi_2S_3)} \qquad (4)$$

$$C^2_{H^+} \times C_{S^{=}} = K_{(H_2S)} \qquad (2)$$

Cubing (2) and then dividing it into (4),

$$\frac{C^2_{Bi^{+++}}}{C^6_{H^+}} = \frac{K_{(Bi_2S_3)}}{K^3_{(H_2S)}}$$

$$C_{Bi^{+++}} = \sqrt{\frac{K_{(Bi_2S_3)} \times C^6_{H^+}}{K^3_{(H_2S)}}}$$

By applying the above principle it is possible to calculate the H^+ ion concentration which must be maintained in a solution in order to prevent the precipitation of a given quantity of a metallic ion as sulfide.

Example 2. What quantity of Mn^{++} ion remains unprecipitated when 100 ml. of a 0.3 *M* HNO_3 solution is saturated with H_2S? Assume that the green variety of MnS is formed. The $K_{s.p.}$ of MnS (green) is 6.2×10^{-22}.

$$C_{Mn^{++}} \times C_{S^{=}} = 6.2 \times 10^{-22}$$

From example 1, $C_{S^{=}} = 1.5 \times 10^{-22}$. Substituting this value in the solubility-product equation for MnS, we get

$$C_{Mn^{++}} = \frac{6.2 \times 10^{-22}}{1.5 \times 10^{-22}} = 4.1 \text{ gram-ion per liter}$$

Converting to gram concentration,

$$C_{Mn^{++}} = 4.1 \times 55 = 226 \text{ g. per liter}$$

Hence 22.6 g. of Mn^{++} ion remain in solution upon saturating with H_2S, 100 ml. of a 0.3 *M* HNO_3 solution containing Mn^{++} ions.

Example 3. What H^+ ion concentration is required to prevent any NiS from precipitating when a solution containing 0.5 g. of Ni^{++} ion per 100 ml. is saturated with H_2S? $K_{(NiS)} = 1.4 \times 10^{-24}$ and $K_{(H_2S)} = 1.1 \times 10^{-23}$.

The solution contains 5 g. Ni^{++} ion per liter. At. wt. Ni = 58.7.

$$C_{Ni^{++}} = \frac{5}{58.7} = 0.085 \text{ gram-ion per liter}$$

$$C_{Ni^{++}} \times C_{S^{=}} = 1.4 \times 10^{24} \qquad (1)$$

$$C^2_{H^+} \times C_{S^{=}} = 1.1 \times 10^{2} \qquad (2)$$

Dividing (1) by (2), we get

$$\frac{C_{Ni^{++}}}{C^2_{H^+}} = \frac{1.4 \times 10^{-24}}{1.1 \times 10^{-23}}$$

$$C^2_{H^+} = \frac{1.1 \times 10^{-23} \times C_{Ni^{++}}}{1.4 \times 10^{-24}} \qquad (3)$$

$$= \frac{1.1 \times 10^{-23} \times 0.085}{1.4 \times 10^{-24}}$$

$$= \frac{93.5 \times 10^{-26}}{1.4 \times 10^{-24}}$$

$$= 67 \times 10^{-2}$$

$$C_{H^+} = \sqrt{67 \times 10^{-2}} = 0.82 \text{ gram-ion per liter}$$

PROBLEMS

1. At 25° C. and under 1 atmosphere of pressure, H_2S dissolves in water to the extent of about 0.1 gram-mol per liter. By experiment the $S^=$ ion concentration was found to be 1.2×10^{-15} gram-ion. What would be the $S^=$ ion concentration in a 0.3 M H^+ ion solution? $C^2_{H^+} \times C_S = 1.1 \times 10^{-23}$.

Ans. 1.2×10^{-22} gram-ion per l.

2. A 3 M H^+ ion solution is saturated with H_2S. Calculate the $S^=$ ion concentration.

Ans. 1.2×10^{-24} gram-ion per l.

3. H_2S is passed into a solution containing 1×10^{-8} gram-ion of Cd^{++} ion and 0.3 gram-ion of H^+ ion per liter. Will CdS be precipitated when the solution becomes saturated with H_2S? $K_{s.p.}$ of CdS is 3.8×10^{-28} and $C^2_{H^+} \times C_S = 1.1 \times 10^{-23}$.

Ans. No.

4. Substitute in problem 3 a Cd^{++} ion concentration of 1×10^{-7} gram-ion per liter and show by calculation whether or not CdS will precipitate.

5. Calculate the minimum concentration of Cd^{++} ion which will satisfy the solubility product of CdS in a liter of solution containing a $S^=$ ion concentration of 1.2×10^{-22}.

Ans. 3.2×10^{-6} gram-ion per l.

6. It is desired to separate the copper and tin group metals from a solution containing zinc. What is the maximum Zn^{++} ion concentration that may be present in the solution without causing precipitation of some ZnS, when H_2S is passed in until the saturation point is reached, the final acidity of the solution being 0.3 M with respect to H^+ ion?

Ans. 5.4×10^{-4} gram-ion per l.

7. In problem 6, suppose that the initial acidity of the solution had been 0.3 M and that in the course of precipitating the copper and tin group sulfides the acidity increased to 0.9 M upon reaching the H_2S saturation point. (*a*) Explain why the acidity increased. (*b*) Calculate the milligrams of Cd^{++} ion that would remain in 100 ml. of solution at a final acidity of 0.9 M. (*c*) How many milligrams of Zn^{++} ion may be present without danger of ZnS precipitating?

Ans. (*b*) 0.31 mg.
(*c*) 32 mg.

8. A liter solution containing 0.05 gram-ion quantities of Cu^{++}, Hg^{++}, Bi^{+++}, Co^{++}, and Ni^{++} ions is saturated with H_2S, the final acidity being

0.3 M. Which $K_{s.p.}$ values are exceeded? See solubility-product tables on pages 98–100.

9. One hundred milliliters of a dilute acid solution contains 25 mg. of each of the following ions: Pb^{++}, As^{+++}, Sn^{++}, Mn^{++}, and Fe^{++}. The solution is saturated with H_2S, the final acidity being 0.3 M. Which $K_{s.p.}$ values are exceeded? See solubility-product tables on pages 98–100.

10. A solution containing 0.01 gram-ion of Mg^{++} per liter is made alkaline with NH_4OH. What is the maximum OH^- ion concentration which can be present without $Mg(OH)_2$ precipitating? $K_{s.p.}$ of $Mg(OH)_2$ is 3.4×10^{-11}.
Ans. 5.8×10^{-5} gram-ion per l.

11. If the solution in problem 10 is made 0.2 M in NH_4OH, how much NH_4^+ ion must be added so as to maintain the OH^- ion concentration just below the point at which $Mg(OH)_2$ will precipitate? The 0.2 M NH_4OH is 1.2 per cent ionized.
Ans. 5.8×10^{-2} gram-ion per l.

12. "Magnesia mixture" is an ammoniacal solution of either magnesium and ammonium chlorides, or magnesium and ammonium nitrates. Calculate the grams of NH_4NO_3 which must be added to prevent $Mg(OH)_2$ precipitating when a solution of magnesia mixture is prepared from 130 g. $Mg(NO_3)_2 \cdot 6H_2O$ and 35 ml. of 6 M NH_4OH, plus enough water to make 1 liter. Assume complete ionization of the salts. $K_{s.p.}$ of $Mg(OH)_2$ is 3.4×10^{-11}.
Ans. 36 g.

13. One hundred milliliters of a solution containing 5 ml. of 6 M HNO_3, 10 mg. of Cu^{++} ion, and 10 mg. of Fe^{++} is saturated with H_2S. Will CuS precipitate? Will FeS precipitate? $C^2_{H^+} \times C_{S^{--}} = 1.1 \times 10^{-23}$.

14. A solution contains 100 mg. of Zn^{++} ions per liter and is 0.01 M in $HC_2H_3O_2$ which is 4.2 per cent ionized. Will ZnS precipitate when the solusion is saturated with H_2S? $K_{s.p.}$ of $ZnS = 6.6 \times 10^{-26}$.

15. A 1 M solution of $HC_2H_3O_2$ (0.4 per cent ionized) contains 100 mg. of Mn^{+++} ion per liter. How many grams of $NH_4C_2H_3O_2$ may be added to a liter of the solution before MnS will precipitate when the solution is saturated with H_2S? $K_{s.p.}$ of $MnS = 7.0 \times 10^{-16}$.
Ans. 270 g.

Case 23. Precipitations involving two solubility product constants: Fractional precipitation.

In the preceding discussion of the solubility-product principle we considered the precipitation of only a single compound. For example, AgCl is precipitated by adding a solution of Cl^- ions to one containing Ag^+ ions, and *vice versa.* In the separation of ions into groups several different kinds of ions are caused to form slightly soluble compounds by the addition of a group reagent, i.e., some ion which will combine with certain other ions to form slightly soluble compounds. Thus Ag^+, Hg_2^{++}, and Pb^{++} ions are precipitated as the respective chlorides by the addition of an excess of Cl^- ions. The copper and tin groups are precipitated from 0.3 N H^+ ion solution by the addition of an excess of $S^=$ ions. The iron and aluminum groups are precipitated as sulfides (and hydroxides) in alkaline solution. The alkaline earth metals are separated as carbonates, leaving the alkali metals in solution. The simultaneous precipitation of two or more compounds by adding a reagent is called **fractional precipitation.** If the salts precipitated independently of each other, just as they do in pure water, then fractional precipitation calculations would be very simple. Unfortunately, only a relatively few precipitates are formed independently of other precipitates. Common examples are: (1) the silver halides, AgCl, AgBr, and AgI; (2) silver chloride and silver chromate; and (3) the sulfides of antimony and tin. Most of the slightly soluble salts do not behave independently, and hence the solubility-product principle can be applied only approximately to most fractional precipitations. Such phenomena are complex, and at present our knowledge of the mechanism is but slight. Precipitations of this type were discussed in Chapter XII under the heading of "Co-precipitation" (page 102).

Let us now consider an example of fractional precipitation where two slightly soluble salts behave independently of each other. If we add dropwise, and with continuous stirring, a dilute solution of silver nitrate to a solution containing equivalent quantities of a soluble chloride and a soluble bromide, AgBr will precipitate first, as its value of $K_{\text{s.p.}}$ is smaller than that of AgCl. Silver bromide will continue to precipitate until the $K_{\text{s.p.}}$ of AgCl is just exceeded and then AgCl will begin to precipitate along with AgBr. From this point on, both AgBr and AgCl precipitate together. When equilibrium is established in the saturated solution, the solubility-product relations of AgBr and AgCl must hold simultaneously.

$$C_{\mathrm{Ag}^+} \times C_{\mathrm{Br}^-} = K_{(\mathrm{AgBr})} = 4 \times 10^{-13} \tag{1}$$

$$C_{\mathrm{Ag}^+} \times C_{\mathrm{Cl}^-} = K_{(\mathrm{AgCl})} = 1.1 \times 10^{-10} \tag{2}$$

The concentration of the silver ions, C_{Ag^+}, will have the same value in both equations, since it is the **total** silver ion concentration of the solution saturated with respect to both AgBr and AgCl.

Hence, dividing (1) by (2) we obtain the equilibrium ratio of the Br^- ion and Cl^- ion concentrations:

$$\frac{C_{Br^-}}{C_{Cl^-}} = \frac{4 \times 10^{-13}}{1.1 \times 10^{-10}} = 3.6 \times 10^{-3}$$

Therefore the Br^- ion concentration is 3.6×10^{-3} times that of the Cl^- ion when the two salts are precipitating simultaneously. Otherwise stated, the Cl^- ion concentration is about 300 times the Br^- ion concentration.

When $\frac{C_{Br^-}}{C_{Cl^-}} > \frac{1}{300}$, the value of the fraction must be lowered in order to reach the equilibrium ratio. Hence, upon adding Ag^+ ions to such a solution, AgBr precipitates until the Br^- ion concentration is $\frac{1}{300}$ that of the Cl^- ion concentration.

When $\frac{C_{Br^-}}{C_{Cl^-}} < \frac{1}{300}$, Cl^- ions will precipitate first as AgCl, upon adding Ag^+ ions, until the concentration of Cl^- ions is 300 times that of the Br^- ions.

If $\frac{C_{Br^-}}{C_{Cl^-}} = \frac{1}{300}$, then upon adding Ag^+ ions both Br^- and Cl^- ions precipitate simultaneously in the ratio of one gram-ion of Br^- to about 300 gram-ions of Cl^-.

PROBLEMS

1. K_2CrO_4 solution is added drop by drop to a solution containing 10 mg. of Pb^{++} ion and 10 mg. of Ba^{++} ion. Which chromate will precipitate first? $K_{S.P.}$ of $PbCrO_4 = 1.8 \times 10^{-14}$. $K_{S.P.}$ of $BaCrO_4 = 2.3 \times 10^{-10}$.

Ans. $PbCrO_4$.

2. In a solution containing 1 mg. of Pb^{++} ion and 500 mg. of Ba^{++} ion, which chromate will precipitate first when K_2CrO_4 solution is added dropwise?

Ans. $PbCrO_4$.

3. Calculate the equilibrium ratio of $\frac{C_{Ba^{++}}}{C_{Sr^{++}}}$ in a solution saturated with both $BaSO_4$ and $SrSO_4$. $K_{S.P.}$ of $BaSO_4 = 1.2 \times 10^{-10}$. $K_{S.P.}$ of $SrSO_4 = 2.8 \times 10^{-7}$.

Ans. 4.3×10^{-4}.

4. (*a*) Explain what will happen when H_2SO_4 is added to a solution containing Ba^{++} and Ca^{++} ions in relative concentration equal to the $\frac{C_{Ba^{++}}}{C_{Sr^{++}}}$

ratio calculated in problem 4. (*b*) What would happen upon adding H_2SO_4, if the relative concentration of these ions is greater than the equilibrium ratio? (*c*) Explain what would happen upon adding H_2SO_4 to a solution having a relative concentration of Ba^{++} ions to Ca^{++} ions less than the equilibrium ratio.

5. (*a*) In a solution saturated with both AgBr and AgCl, what is the ratio of Br^- ion to Cl^- ion? (*b*) What is the ratio of I^- ion to Br^- ion in a solution saturated with both AgI and AgBr? (*c*) Calculate the equilibrium ratio $\frac{C_{I^-}}{C_{Cl^-}}$ in a solution saturated with both AgI and AgCl. $K_{s.p.}$ of AgCl $= 1.1 \times 10^{-10}$. $K_{s.p.}$ of AgBr $= 4.0 \times 10^{13}$. $K_{s.p.}$ of AgI $= 1.5 \times 10^{-16}$.

Ans. (*a*) 3.6×10^{-3}.
(*b*) 3.7×10^{-4}.
(*c*) 1.4×10^{-6}.

CHAPTER XVI

DISSOLVING OF PRECIPITATES

The process of dissolving precipitates is just the reverse of that in the several preceding cases involving the condition required for a precipitate to form; namely, the value of the product of the gram-ion concentrations (each raised to the proper power) must exceed the value of the K_{sp} for the compound in question. Conversely, if by the addition of a reagent the concentration of one or both ions derived from the precipitate is lowered below the saturation value, then the equilibrium will be disturbed, and in order for equilibrium to be re-established, some of the precipitate will dissolve. If a sufficient excess of reagent is added, all the precipitate will go into solution. There are six different ways by which ions can be removed from saturated solutions of compounds by the addition of certain reagents. These may be listed as follows:

1. By the formation of a less ionized product.
2. By the formation of a weakly ionized and slightly soluble gas.
3. By the formation of a complex ion.
4. By converting an amphoteric compound into a soluble salt by adding an excess of either a strong acid or a strong base.
5. By oxidizing or reducing one of the ions.
6. By the formation of a complex ion and simultaneously oxidizing another ion.

Any one of these reactions will disturb the equilibrium in a saturated solution in contact with the solid of a slightly soluble electrolyte and hence will cause more solid to go into solution. Since compounds differ widely in their chemical nature, certain of them will require one solution process while others will require different methods.

All the above solution processes involve ionic equilibria in aqueous solutions. Although water is the most common solvent, it must be remembered that there are other solvents, for example, alcohol, ether, chloroform, carbon tetrachloride, carbon bisulfide, and glacial acetic acid. The ionization relationships must be determined for each solvent. In general, an inorganic substance is more soluble in water than in an organic solvent, but there are exceptions. For example, sulfur is insoluble in water but highly soluble in carbon bisulfide. Again, bromine and iodine are only slightly soluble in water but have high solubilities in organic liquids such as alcohol and carbon tetrachloride. As a rule, organic substances are more soluble in organic liquids than they are in water. Often mixed solvents are more effective than the pure liquids.

1. Dissolving a precipitate by forming a less ionized product. Example: Dissolving calcium oxalate in hydrochloric acid.

Calcium oxalate in equilibrium with its ions in a saturated solution is expressed by the equation:

$$\underset{\text{(Solid)}}{CaC_2O_4} \rightleftharpoons Ca^{++} + C_2O_4^{=}$$

The $K_{\text{s.p.}}$ of CaC_2O_4 is

$$C_{Ca^{++}} \times C_{C_2O_4} = 2.6 \times 10^{-9}$$

Upon adding HCl, a highly ionized acid, to the saturated calcium oxalate solution the H^+ ion concentration is greatly increased and hence $H_2C_2O_4$ is formed since this acid is very much less ionized than HCl. Thus $C_2O_4^{=}$ ions are removed from the solution and more solid CaC_2O_4 must dissolve in order to maintain the $C_2O_4^{=}$ ion concentration required by the $K_{\text{s.p.}}$ of CaC_2O_4. By adding sufficient HCl all the CaC_2O_4 will dissolve. The Ca^{++} ions and Cl^- ions will not combine to any great extent as $CaCl_2$ is a highly ionized salt. The equilibria involved may be expressed in the following way:

$$\begin{array}{rcl}
\underset{\text{(Solid)}}{CaC_2O_4} \rightleftharpoons Ca^{++} + & C_2O_4^{=} & \\
HCl \rightleftharpoons Cl^{-} + & H^{+} & \\
 & \downarrow\uparrow & \\
 & HC_2O_4^{-} & \text{(Very weakly ionized)} \\
\underset{\text{(Highly ionized)}}{HCl \rightleftharpoons Cl^{-}} + & H^{+} & \\
 & \downarrow\uparrow & \\
 & H_2C_2O_4 &
\end{array}$$

$K_{\text{(ion)}}$ of $H_2C_2O_4 = 3.8 \times 10^{-2}$

$K_{\text{(ion)}}$ of $HC_2O_4^{-} = 5 \times 10^{-5}$

The ionization of HCl is too high to yield an ionization constant.

Will calcium oxalate dissolve in acetic acid? The ionization constant of acetic acid is 1.8×10^{-5}. Therefore this acid is too weakly ionized to yield sufficient H^+ ion to cause the formation of the weaker ionized $HC_2O_4^-$ ion. Hence, calcium oxalate will not dissolve in acetic acid.

2. Dissolving a precipitate by forming a weakly ionized and slightly soluble gas. Example: dissolving manganese sulfide in hydrochloric acid.

A saturated aqueous solution of MnS in equilibrium with solid MnS is represented in the following way:

$$\underset{\text{(Solid)}}{\text{MnS}} \rightleftharpoons \text{Mn}^{++} + \text{S}^{=}$$

In this solution the following condition is maintained:

$$C_{\text{Mn}^{++}} \times C_{\text{S}^{=}} = K_{\text{s.p.}} \text{ of MnS}$$

In order to dissolve MnS it will be necessary to lower the product of the gram-ion concentrations of Mn^{++} ions and $S^{=}$ ions until it is numerically less than the solubility-product constant for MnS. This may be accomplished by lowering the concentration of either or both of the ions. Upon adding HCl to MnS, the following equilibria are set up:

$$\begin{array}{lcl}
\underset{\text{(Solid)}}{\text{MnS}} \rightleftharpoons \text{Mn}^{++} + & \boxed{\begin{array}{c}\text{S}^{=}\\[2ex] \text{H}^{+}\end{array}} & \\
\text{HCl} \rightleftharpoons \text{Cl}^{-} & & \\
& \downarrow\uparrow & \\
& \boxed{\begin{array}{c}\text{HS}^{-}\\[2ex] \text{H}^{+}\end{array}} & \\
\text{HCl} \rightleftharpoons \text{Cl}^{-} \quad + & & \rightleftharpoons \underset{\text{(Dissolved)}}{\text{H}_2\text{S}} \rightleftharpoons \underset{\text{(Gas)}}{\text{H}_2\text{S}} \uparrow
\end{array}$$

Mn^{++} ions and Cl^- ions do not combine to any great extent as $MnCl_2$ is a highly ionized salt. The H^+ ions and $S^=$ ions, on the other hand, combine to form successively HS^- and H_2S. H_2S is a slightly soluble gas, and a saturated aqueous solution of it contains only about 0.1 mol per liter. Moreover, H_2S is a very weak dibasic acid. Instead of considering each ionization of H_2S separately, it will simplify the discussion to use the combined equations for the two ionization constants, K_1 and K_2, and to modify the latter to $C^2_{H^+} \times C_{S^=} = K_{(H_2S)}$. Some of the H^+ ions from the dissociation of HCl combine with $S^=$ ions from the MnS to form the slightly soluble H_2S gas and weakly dissociated H_2S and HS^-. Thus the $S^=$ ion concentration is lowered to an exceedingly small value, a value very much less than that given by MnS in its saturated aqueous solution. The removal of some of the $S^=$ ions from the solution will lower the product of $C_{Mn^{++}}$ and $C_{S^=}$ to a value less than that of the $K_{s.p.}$ of MnS, and consequently more MnS must dissolve until the $K_{s.p.}$ for MnS is again reached. But this $S^=$ ion concentration is greater than that required to satisfy the condition $C^2_{H^+} \times C_{S^=} = K_{(H_2S)}$, and hence more H_2S is formed, thus again lowering the product of $C_{Mn^{++}}$ and $C_{S^=}$ below the $K_{s.p.}$ for MnS, and more MnS must dissolve. As the MnS dissolves, the concentration of Mn^{++} ion increases. Since the solubility of MnS in a solution of Mn^{++} ions is less than it is in pure water (common-ion effect), it is evident that, as the MnS dissolves, the $S^=$ ion concentration progressively diminishes. If only H^+ ions from the H_2S were present in the solution, the $S^=$ ion concentration required to satisfy its equilibrium value would soon be reached and the dissolving of MnS would then stop. However, by maintaining a high concentration of H^+ ion by using an excess of a strong acid such as HCl, the concentration of the $S^=$ ion in the solution is kept below the value required to satisfy the $K_{s.p.}$ of MnS, and consequently the reaction proceeds until all the MnS is dissolved. Or we may say that MnS dissolves in HCl because the $S^=$ ion concentration in a saturated aqueous solution of MnS is greater than the $S^=$ ion concentration required to satisfy the equilibrium expression $C^2_{H^+} \times C_{S^=} = K_{(H_2S)}$. In an excess of a strong acid such as HCl, the equilibrium $C_{S^=}$ value is very low. Hence, in the presence of MnS, which has a relatively large solubility in water, the low value of $C_{S^=}$ is always exceeded and consequently the reaction proceeds in the presence of an excess acid until all the MnS is dissolved. The same explanation applies to the solubility of the other sulfides of the aluminum and iron groups (FeS, CoS, NiS, and ZnS) in strong acids. The sulfides of aluminum and chromium hydrolize in aqueous solution, forming very slightly soluble hydrous oxides, $Al_2O_3 \cdot xH_2O$ and $Cr_2O_3 \cdot xH_2O$, the degree of hydration depending upon various conditions under which they are formed. Upon adding an excess of a strong acid, these hydrous oxides dissolve, owing to the formation of soluble salts.

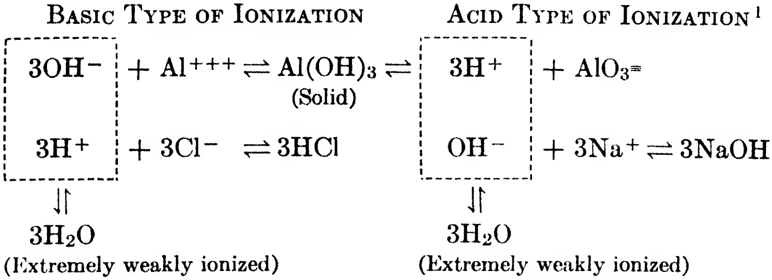
The solubilities of the sulfides of the copper and tin groups are so small that in their saturated aqueous solutions the $S^{=}$ ion concentration is either less than, or only slightly greater than, the value required to satisfy the equilibrium condition $C^2_{H^+} \times C_{S^=} = K_{(H_2S)}$. In the presence of an excess of a highly ionized acid, the value of $C_{S^=}$ is of course greatly lowered. Consequently, when only a very small amount of a sulfide such as CuS has dissolved, the equilibrium value of $C_{S^=}$ is reached and further solution ceases. The very slight solubility of CuS in HCl may be expressed by the following ionic equilibria:

$$\begin{array}{lcl}
CuS \rightleftharpoons Cu^{++} + & \begin{array}{|c|}\hline S^{=} \\ \\ H^{+} \\ \hline\end{array} & \\
HCl \rightleftharpoons Cl^{-} \quad + & & \\
 & \downarrow\uparrow & \\
HCl \rightleftharpoons Cl^{-} \quad + & \boxed{H^{+}\,HS^{-}} & \rightleftharpoons \underset{\text{(Dissolved)}}{H_2S} \rightleftharpoons \underset{\text{(Gas)}}{H_2S}\uparrow
\end{array}$$

To sum up, the solution of a sulfide in an acid depends on two factors: (1) the solubility of the sulfide in water, and (2) the concentration and degree of ionization of the acid. The latter determines the H^+ ion concentration, which in turn fixes the $S^{=}$ ion concentration that can exist with it. This relationship is expressed by the equation $C^2_{H^+} \times C_{S^=} = K_{(H_2S)}$. The value of $C_{S^=}$ is the equilibrium $S^{=}$ ion concentration, and this of course varies with the acid concentration. Hence, for a given H^+ ion concentration, the solution of a sulfide will depend upon its solubility in water. Sulfides such as FeS, MnS, and ZnS dissolve readily and completely in an excess of HCl, since the $S^{=}$ ion concentration in their saturated aqueous solutions is greater than the equilibrium value of $C_{S^=}$ required by the equation $C^2_{H^+} \times C_{S^=} = K_{(H_2S)}$. Sulfides like CuS dissolve only to a slight extent in HCl, since they yield $S^{=}$ ion concentrations only slightly greater than the equilibrium value $C_{S^=}$. The $S^{=}$ ion concentration in the saturated aqueous solutions of sulfides such as HgS is less than the equilibrium value $C_{S^=}$, and therefore these sulfides will not dissolve at all in HCl. The solvent action of HNO_3, an oxidizing agent as well as an acid, will be discussed subsequently (see page 164).

3. Dissolving a precipitate by forming a complex ion. Examples of this process of solution will be given subsequently in the discussion of complex-ion equilibria (see page 182).

4. Dissolving a precipitate of an amphoteric substance by an excess of either a strong acid or a strong base. Example: dissolving aluminum hydroxide in hydrochloric acid or sodium hydroxide. The equilibria are represented graphically as follows:



BASIC TYPE OF IONIZATION ACID TYPE OF IONIZATION[1]

$$\begin{array}{llll}
\boxed{\begin{array}{c} 3OH^- \\ \\ 3H^+ \end{array}} & \begin{array}{l} + Al^{+++} \rightleftharpoons \underset{\text{(Solid)}}{Al(OH)_3} \rightleftharpoons \\ \\ + 3Cl^- \rightleftharpoons 3HCl \end{array} & \boxed{\begin{array}{c} 3H^+ \\ \\ OH^- \end{array}} & \begin{array}{l} + AlO_3^{\equiv} \\ \\ + 3Na^+ \rightleftharpoons 3NaOH \end{array} \\
\downarrow\uparrow & & \downarrow\uparrow & \\
3H_2O & & 3H_2O & \\
\text{(Extremely weakly ionized)} & & \text{(Extremely weakly ionized)} &
\end{array}$$

Note that in both types the solvent action is due to the formation of the extremely weakly ionized compound water. The HCl lowers the OH^- concentration resulting from the basic type of ionization of the amphoteric $Al(OH)_3$, and NaOH lowers the H^+ ion concentration due to the acid type of ionization. The two types of ionization are represented by the following equilibrium constants:

$$\underset{\text{(As base)}}{K_{\text{(Ion)}}} = \frac{C_{Al^{+++}} \times C^3_{OH^-}}{C_{Al(OH)_3}} \tag{1}$$

$$\underset{\text{(As acid)}}{K_{\text{(Ion)}}} = \frac{C^3_{H^+} \times C_{AlO_3^{\equiv}}}{C_{H_3AlO_3}} \tag{2}$$

It must be pointed out that the numerical values of K_b and K_a are not the same, as that would mean that aluminum hydroxide ionizes to the same extent both as an acid and as a base. As a matter of fact, the basic ionization of this compound is more pronounced than the acid. With other amphoteric hydroxides the reverse is sometimes true. The solvent action of weak acids and

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[1] H_3AlO_3 loses some of its water and its ionization may be written thus: $H_3AlO_3 \rightleftharpoons H_2O + HAlO_2 \rightleftharpoons H^+ + AlO_2^-$. For the sake of simplicity, only H_3AlO_3 will be considered.

bases upon amphoteric hydroxides is very slight, since they yield H^+ ion and OH^- ion concentrations not far greater than those furnished by the ionization of water.

Amphoterism and also the degree of acidic and basic ionization of amphoteric hydroxides are related to the position of their metallic elements in the periodic table. If a line be drawn obliquely from Be through Sb in the periodic table, it will be noted that those elements on or near the line form amphoteric hydroxides. If the OH^- ion predominates in the amphoteric ionization the compound is called an hydroxide (e.g., aluminum hydroxide and not aluminic acid). When the H^+ ion predominates the compound is called an acid (e.g., arsenious acid and not arsenious hydroxide). The important point to remember is that an amphoteric compound **always** ionizes simultaneously **both** as an acid and as a base. Hence, amphoteric compounds are both hydroxides and acids. The name amphoteric comes from the Greek word *amphoteros*, which means *both*. It is a common misconception among beginners in chemistry that such a compound ionizes only as a base in the presence of an acid and only as an acid in the presence of a base.

5. Dissolving a precipitate by oxidizing or reducing one of the ions.

On page 162 it was pointed out that CuS does not dissolve in HCl because the $S^{=}$ ion concentration in its saturated aqueous solution is only slightly greater than the $S^{=}$ ion concentration which can exist in equilibrium with the H^+ ion concentration of a strong acid such as HCl. Consequently, after a very small amount of CuS has dissolved, the $S^{=}$ ion concentration reaches a value which satisfies the constant $K_{(H_2S)}$ and then the dissolving stops. In order to dissolve a fairly large quantity of CuS, it is necessary to employ a reaction which will lower the $S^{=}$ ion concentration to a value much lower than that given by a saturated aqueous solution of CuS. This is accomplished by the use of HNO_3, which oxidizes the $S^{=}$ ion to free sulfur. Although this reaction is reversible, it does not reach equilibrium until the $S^{=}$ ion concentration is reduced to a value vastly smaller than the $S^{=}$ concentration in a saturated aqueous solution of CuS. The reaction which takes place when CuS is dissolved in HNO_3 is expressed by the following equations:

$$3CuS \rightleftharpoons 3Cu^{++} + \cancel{3S^{=}} \qquad (1)$$

$$\cancel{3S^{=}} - 6e \rightleftharpoons 3S^{\circ} \qquad (2)$$

$$2NO_3^- + 8H^+ + 6e \rightleftharpoons 2NO + 4H_2O \qquad (3)$$

$$3CuS + 2NO_3^- + 8H^+ \rightleftharpoons 3Cu^{++} + 3S^\circ + 2NO + 4H_2O \qquad (4)$$

In equation (4), $8H^+$ ions are associated with $8NO_3^-$ ions, and since only $2NO_3^-$ ions are reduced, the remaining $6NO_3^-$ ions unite with the $3Cu^{++}$ ions to form $3Cu(NO_3)_2$. Therefore, of the $8HNO_3$ molecules required to complete equation (4), 2 function as an oxidizing agent and 6 as an acid furnishing NO_3^- ions. The completed equation is:

$$3CuS + 8HNO_3 \rightleftharpoons 3Cu(NO_3)_2 + 3S^\circ + 2NO + 4H_2O \qquad (5)$$

The essential reaction is the oxidation of $S^=$ to S° and may be expressed as follows:

$$S^= - 2e \rightleftharpoons S^\circ \qquad (6)$$

Applying the law of mass action to (6), we get

$$\frac{C_{S^=}}{C_{S^\circ}} = K \qquad (7)$$

But since C_{S° is a constant at a given temperature, the equation becomes

$$C_{S^=} = K \times C_{S^\circ} = k \qquad (8)$$

This equation states that, when HNO_3 reacts with a sulfide, equilibrium will be reached when the $S^=$ ion concentration attains a value equal to k. The equilibrium value is an exceedingly small one, much smaller than either the $S^=$ ion concentration in a saturated aqueous CuS solution or the equilibrium $S^=$ ion concentration in the reaction between HCl and a sulfide such as CuS. The $S^=$ ion concentration in a saturated aqueous solution of most sulfides is considerably greater than the equilibrium $S^=$ ion concentration for HNO_3 (equation [8]), and hence these sulfides dissolve readily in HNO_3. Heating greatly increases the rate of solution.

6. Dissolving a precipitate by formation of a complex ion and simultaneously oxidizing another ion.

A saturated aqueous solution of HgS contains an extremely low concentration of $S^=$ ion, and hence when HgS is treated with HNO_3 only a minute amount dissolves. The very small amount of $S^=$ ion thus formed is oxidized to free S°, and hence a little more HgS dissolves. But the $S^{=}$ ion concentration rapidly decreases as the Hg^{++} ion concentration increases (common-ion effect) and quickly reaches a value equal to the equilibrium concentration (equation [8]) at which point reaction ceases. By using *aqua regia* (a mixture of concentrated HCl and concentrated HNO_3) the HgS dissolves readily, owing to an increase in the $S^{=}$ ion concentration above the equilibrium value required in equation (8). The high Cl^{-} ion concentration from the concentrated HCl combines with Hg^{++} ions to form the extremely stable complex ion $HgCl_3^{-}$. This causes a lowering of the Hg^{++} concentration, and consequently as more HgS dissolves, the $S^{=}$ ion concentration exceeds the equilibrium concentration and is oxidized by the concentrated HNO_3. This process causes a lowering of the concentration of both Hg^{++} ions and $S^{=}$ ions, and hence HgS dissolves rapidly. The reactions are expressed by the following equilibria:

$$HgS \rightleftharpoons \cancel{Hg}^{++} + \cancel{S}^{=} \tag{1}$$

$$\cancel{Hg}^{++} + 3Cl^{-} \rightleftharpoons HgCl_3^{-} \tag{2}$$

$$\cancel{S}^{=} + 2NO_3^{-} + 4H^{+} \rightleftharpoons 2NO_2 + 2H_2O + S^{\circ} \tag{3}$$

$$HgS + 2NO_3^{-} + 4H^{+} + 3Cl^{-} \rightleftharpoons HgCl_3^{-} + 2NO_2 + 2H_2O + S^{\circ} \tag{4}$$

Case 24. Dissolving a precipitate by forming a less ionized product. Illustrated in the following problems.

PROBLEMS

1. Explain why the alkaline earth oxalates dissolve in hydrochloric acid but not in acetic acid. *Suggestion:* Write equations representing the equilibria involved, and compare the values of their equilibrium constants.

2. Lead sulfate dissolves in hot concentrated solutions of ammonium acetate or ammonium tartrate. Explain fully. On adding dilute sulfuric acid, lead sulfate is reprecipitated. Explain.

3. If a soluble chromate is added to a solution obtained by dissolving lead sulfate in ammonium acetate solution, lead chromate precipitates. Explain fully.

4. (*a*) One-tenth gram-mol of BaC_2O_4 is dissolved in a liter of 0.2 *M* HCl. Calculate the gram-ion concentration of Ba^{++} ion. (*b*) What is the H^{+} ion concentration, if the $H_2C_2O_4$ is 40 per cent ionized (primary stage)?

Ans. (*a*) 0.1 gram-ion per l.
(*b*) 0.08 gram-ion per l.

Case 25. Dissolving a precipitate by forming a weakly ionized and slightly soluble gas. Illustrated in the following problems.

PROBLEMS

1. Discuss the process of dissolving ZnS in HCl solution. *Suggestion:* Give the ionic changes involved and discuss these in relation to the $K_{\text{s.p.}}$ of ZnS and $K_{(\text{H}_2\text{S})}$.

2. Five-tenths gram-mol MnS is dissolved in a liter of 1 *M* HCl at room temperature. (*a*) How much H_2S is formed? (*b*) How much H_2S escapes from solution? (*c*) If all the H_2S were boiled out of the solution, would the manganese reprecipitate?

Ans. (*a*) 12.2 l. at 25°.
(*b*) 9.8 l. at 25°.

3. Ten milliliters of 6 *M* HCl are poured over 0.5 g. of $MgCO_3$. (*a*) How much HCl remained in excess? How many milligrams of (*b*) $MgCl_2$ and (*c*) CO_2, respectively, are produced?

Ans. (*a*) 8.0 ml.
(*b*) 565 mg.
(*c*) 261 mg.

4. One one-hundredth gram-mol of FeS is added to 100 ml. of 0.2 *M* HCl. Will the FeS completely dissolve?

5. (*a*) In problem 4, what will be the molar concentration of H_2S in the $FeCl_2$ solution, assuming no loss of gas? (*b*) What will be the gram-ion concentration of $S^{=}$ ion?

Ans. (*a*) 0.01 *M*.
(*b*) 0.01 gram-ion.

6. (*a*) How many milliliters of 6 *M* HCl are required to just dissolve 100 mg. of MnS? (*b*) How many milligrams of $MnCl_2$ and H_2S respectively, are formed?

Ans. (*a*) 0.38 ml.
(*b*) 145 mg., 39.1 mg.

7. How many milliliters of 1 *M* HNO_3 are required to just dissolve (*a*) 0.1 g. of $CaCO_3$; (*b*) 0.1 g. of $SrCO_3$; (*c*) 0.1 g. $BaCO_3$?

Ans. (*a*) 2.0 ml.
(*b*) 1.4 ml.
(*c*) 1.0 ml.

Case 26. Dissolving a precipitate of an amphoteric substance by adding an excess of either a strong acid or a strong base. Illustrated in the following problems.

PROBLEMS

1. (*a*) Write an equation showing the amphoteric character of zinc hydroxide. (*b*) What would be the effect on the equilibrium of adding hydro-

chloric acid? Write the equation and explain fully. (*c*) Suppose that sodium hydroxide be used instead of the acid. Explain.

2. (*a*) Show by an equation the amphoteric nature of $Sn(OH)_2$. (*b*) What weight of KOH would be required to dissolve 500 mg. of $Sn(OH)_2$?[2] (*c*) How much HCl would be required to dissolve 500 mg. of $Sn(OH)_2$?[2]

Ans. (*b*) 368 mg.
(*c*) 240 mg.

3. (*a*) Make a list of the metals whose oxides are amphoteric. (*b*) Where are these elements located in the periodic table? (*c*) Are their aqueous solutions hydroxides, or acids, or both? Explain.

4. How much NaOH is theoretically[2] required to dissolve 0.2 g. of each of the following hydroxides: (*a*) $Al(OH)_3$, (*b*) $Cr(OH)_3$, and (*c*) $Zn(OH)_2$?

Ans. (*a*) 0.10 g.
(*b*) 0.078 g.
(*c*) 0.16 g.

Case 27. Dissolving a precipitate by oxidizing or reducing one of the ions. Illustrated in the following problems.

PROBLEMS

1. Explain why copper sulfide is practically insoluble in hydrochloric acid and sulfuric acid but dissolves completely and rapidly in nitric acid.

2. Mercuric sulfide is practically insoluble in strong hydrochloric acid and dissolves in strong nitric acid only upon prolonged boiling. However, in a mixture of these concentrated acids, called *aqua regia,* mercuric sulfide dissolves rapidly. Explain fully. Give equations for the reactions involved.

3. How many milliliters of 6 N HNO_3 (hot) are required to dissolve 100 mg. of each of the following sulfides: (*a*) PbS, (*b*) CuS, (*c*) Bi_2S_3, and (*d*) CdS? Assume that the H_2S formed in these reactions is oxidized only to H_2O and S.

Ans. (*a*) 0.19 ml. (*c*) 0.26 ml.
(*b*) 0.46 ml. (*d*) 0.31 ml.

4. How much free sulfur is formed upon dissolving 0.5 g. of HgS in *aqua regia*? Some of the free sulfur will be oxidized, but this effect may be disregarded in the calculation.

Ans. 0.069 g.

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[2] In practice, a much larger amount than the theoretical is used in order to prevent hydrolysis.

CHAPTER XVII

THE COORDINATION THEORY: COMPLEX IONS

Werner's Coordination Theory. The ordinary valence theory fails to account for the fact that certain atoms or molecules, normally considered as being saturated, still possess sufficient combining power to hold other atoms or molecules firmly. In order to explain this fact, Alfred Werner introduced the conception of **auxiliary** or **secondary valence.** Ordinary valence was termed **primary valence.** According to Werner "even when, to judge by the valence number, the combining power of certain atoms is exhausted, they still possess in most cases the power of participating further in the construction of complex molecules with the formation of very definite atomic linkages. The possibility of this action is to be traced back to the fact that, besides the affinity bonds designated as principal valencies, still other bonds on the atoms, called auxiliary valencies, may be called into action."[1] This idea is called the **theory of auxiliary valences or the coordination theory,** and it has been very useful in the study of compounds of the higher order whose formation cannot be explained by the ordinary valence theory. A "compound of the higher order" is one formed by the union of two or more saturated molecules, that is, molecules whose constituent atoms are all completely satisfied in accordance with the valence theory. For example, two simple chemical compounds AB and CD may combine to form a compound $AB \cdot CD$. Compounds of the $AB \cdot CD$ type were formerly called "molecular compounds," and they play an important rôle in analytical chemistry, as well as in inorganic and organic chemistry. Such compounds are very numerous. A few are given in the following list illustrating several different types:

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[1] Werner, "Neuere Anschauungen auf dem Gebiete der anorganischen Chemie," fourth edition, p. 44, Viegweg, Braunschweig, 1920; see, also, Schwarz (translated by Bass), "The Chemistry of the Inorganic Complex Compounds," p. 9, John Wiley & Sons, New York, 1922.

Complex Metal-Ammines

General Type: $[Me]NH_3)_6]^{++}X_2^-$, in which Me represents a bivalent metal, e.g., Cu, Cd, Co, Ni, Fe, Zn, etc., and X is a monovalent atom or radical—

$$[Ni(NH_3)_6]^{++}Cl_2^-.$$

$$[Zn(NH_3)_6]^{++}Cl_2^-.$$

General Type: $[Me(NH_3)_6]^{+++}X_3^-$, in which Me represents a trivalent metal, e.g., Co, Cr, Fe, Rh, Bi, etc.—

$$[Co(NH_3)_6]^{+++}Cl_3^-.$$

$$[Cr(NH_3)_6]^{+++}Cl_3^-.$$

General Type: $[Me(NH_3)_6]^{++++}X_4^-$, in which Me represents a quadrivalent metal, e.g., Pt, Si, Sn, etc.—

$$[Pt(NH_3)_6]^{++++}Cl_4^-.$$

$$[Si(NH_3)_6]^{++++}Cl_4^-.$$

General Type: $[Me(NH_3)_4]^{++}X_2^-$, in which Me represents a bivalent metal, e.g., Cu, Cd, Zn, Pt, etc.—

$$[Cu(NH_3)_4]^{++}Cl_2^-.$$

$$[Zn(NH_3)_4]^{++}Cl_2^-.$$

Complex Metal-Cyanides

General Types: $X^+[Me(CN)_2]^-$; $X_2{}^+[Me(CN)_4]^{--}$; $X_3{}^+[Me(CN)_6]^{---}$.

$$K^+[Ag(CN)_2]^-$$

$$K_2{}^+[Cd(CN)_4]^{--}$$

$$K_3[Fe(CN)_6]^{---}.$$

Complex Metal-Sulfides

General Types: $X_2{}^+[MeS_2]^{--}$; $X_3{}^+[MeS_3]^{---}$; $X_3{}^+[MeS_4]^{---}$.

$$K_2{}^+[HgS_2]^{--}$$

$$K_3{}^+[AsS_3]^{---}$$

$$K_3{}^+[AsS_4]^{---}$$

COMPLEX METAL-HALIDES

General Type: $X_2{}^{+}[Me\mathrm{Cl}_3]^{--}$; $X_2{}^{+}[Me\mathrm{Cl}_4]^{--}$; $X_2{}^{+}[Me\mathrm{Cl}_6]^{--}$.

$K_2{}^{+}[AgCl_3]^{--}$

$K_2{}^{+}[PbCl_4]^{--}$

$K_2{}^{+}[PtCl_6]^{--}$.

COMPLEX METAL-THIOCYANATES

General Type: $X_2{}^{+}[Me(\mathrm{CNS})_4]^{--}$, e.g., $K_2{}^{+}[Hg(CNS)_4]^{--}$.

Complex metal salts are also formed with the inorganic radicals: NO_2, NO_3, CO_3, SO_3, SO_4, S_2O_3, etc., as well as with a number of organic radicals; e.g., oxalate, citrate, tartrate, etc.

HYDRATES

Examples: $FeCl_3 \cdot 6H_2O$, $MgCl_2 \cdot 6H_2O$, $CaCl_2 \cdot 6H_2O$ and H_2SO_4 or $SO_3 \cdot H_2O$.

DOUBLE SALTS

Examples: $KAuCl_4$, $K_2Al_2(SO_4)_4$, and $KMgCl_3$, which may also be written $KCl \cdot AuCl_3$, $K_2SO_4 \cdot Al_2(SO_4)_3$, and $KCl \cdot MgCl_2$, respectively.

All the above types of compounds (metal ammines, metal cyanides, etc., hydrates, and double salts) are formed in the same manner, and their differences are apparent only when they are dissolved in water. Upon dissolving in water, some of these compounds show considerable stability; others completely decompose (dissociate). To the former class belong the true **complex salts,** and to the latter the true **double salts.** However, there are many examples of intermediate stages between the completely stable salts and the completely decomposed ones. Hence, there is no sharp distinction between complex salts and double salts. The difference is merely one of degree.

In the above compounds, for example, the metal ammines, it will be observed that one atom functions as a nucleus to which are attached (by auxiliary valences) four or six radicals, thus forming a group called a **complex nucleus** (see Figs. 7 and 8). The radicals attached by auxiliary, or secondary, valence are called **coordinated** groups, and the number of such groups is called the **coordination number.** Hence, the term "coordination theory." The maximum coordination number shows how many groups it is possible for the inner element to hold. For the majority of the metals, this number is six, and for the non-metals, e.g., sulfur, phosphorus, carbon, nitrogen, and boron, it is four.

The atoms or radicals outside the nucleus are attached by ordinary valence to the whole molecule. As this union is weak, such atoms or radicals are readily split off (ionized) in aqueous solution. Hence, these unions are called ionizable linkages.

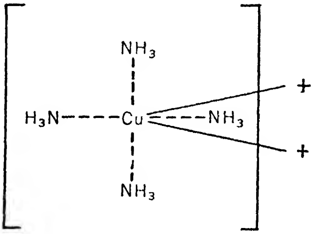

FIG. 7

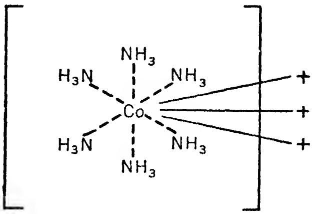

FIG. 8

The coordination number is independent of the nature of the radicals or molecules attached to the central atom; that is, its value is the same whether neutral water molecules, acid radicals (e.g., Cl^-, Br^-, I^-, CN^-, etc.), hydroxyl groups, oxygen atoms, or ammonia molecules are present. Each of these radicals or molecules occupies only one coordination position. In multivalent radicals (e.g., $C_2O_4^=$, $CO_3^=$, $SO_4^=$, etc.), either one or two positions may be occupied.

In general, the tendency to form the central atom of a complex nucleus **increases** with **decreasing** electrical potential; i.e., very few alkali metals, which are at the top of the electromotive series (see page 248), form complex compounds, whereas the majority of the compounds of the noble metals, which are at the bottom of the e.m.f. series, are complex.

There is no difference between the principal valences (i.e., ordinary valences of the valence theory) and auxiliary or secondary valences. The central atom in a complex nucleus possesses an equally divided sum of forces which is numerically expressed by its coordination number. The complex nucleus may be electrically neutral, positive, or negative. For example, in the well-known salt, potassium chloroplatinate $K_2{}^+[PtCl_6]^=$, so often used in analytical chemistry procedures, the complex group functions as a negative ion, and in the blue copper ammonia salt, $[Cu(NH_3)_4]^{++}SO_4{}^=$, known to all students in qualitative analysis, the complex group forms a positive ion. The regularities shown in the following series of various platinum complexes holds good for all complex compounds. Denoting the valence of the complex nucleus by W, the valence of its central atom by V, and the number of univalent acid radicals in it by R, we have:

FORMULA	COMPLEX ION	$V - R = W$
I. $[Pt(NH_3)_6]Cl_4$	Quadrivalent cation	$4 - 0 = +4$
II. $[Pt(NH_3)_5Cl]Cl_3$	Tervalent cation	$4 - 1 = +3$
III. $[Pt(NH_3)_4Cl_2]Cl_2$	Bivalent cation	$4 - 2 = +2$
IV. $[Pt(NH_3)_3Cl_3]Cl$	Univalent cation	$4 - 3 = +1$
V. $[Pt(NH_3)_2Cl_4]$	Neutral	$4 - 4 = 0$
VI. $[Pt(NH_3)Cl_5]K$	Univalent anion	$4 - 5 = -1$
VII. $[PtCl_6]K_2$	Bivalent anion	$4 - 6 = -2$

The Electrolytic Dissociation of Complex Salts. By means of a study of the electrolytic dissociation of complex salts in aqueous solution it is possible to determine whether the complex nucleus is acidic, basic, or neutral in character. "The molecular conductivities of all salts dissociating into the same number of ions are quite close together in numerical value and are unmistakably different from those of other salts giving a different number of ions. At 1000 l. dilution and 25° C., for binary electrolytes (NaCl, KCl) the value is about 125, for ternary ($BaCl_2$, $CaCl_2$, $MgBr_2$) about 250, and for quaternary ($AlCl_3$, $FeCl_3$) about 425. . . . In a similar manner, by measurement of the conductivities of many complex compounds, the correctness of the formulae assigned to them has been proved. At the same time, the agreement found has afforded an additional confirmation of the Coordination Theory." [2] We have just listed a series of seven hexammine salts of platinum by the successive replacement of one to six molecules of ammonia by chlorine. The resulting types may be designated as follows:

[2] Schwarz (translated by Bass), *op. cit.*, p. 22.

Monacido-pentammine,	$[Me(NH_3)_5X]X_3$
Diacido-tetrammine,	$[Me(NH_3)_4X_2]X_2$
Triacido-triammine,	$[Me(NH_3)_3X_3]X$
Tetracido-diammine,	$[Me(NH_3)_2X_4]$
Pentacido-monammine,	$[Me(NH_3)X_5]Me^I$
Hexacido,	$[MeX_6]Me_2$

The acid radicals generally found in complex compounds are: Cl, Br, I, CN, CNS, NO_2, NO_3, SO_3, SO_4, CO_3, and C_2O_4.

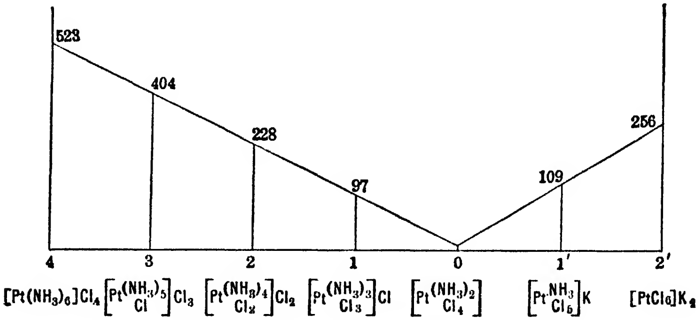

FIG. 9.—Molar Conductivity at 1000 liters Dilution

As an example of the step-by-step transformation of one group into another, we reproduce in Fig. 9 a diagram by Schwarz and Bass[3] based on the molar conductivities of the platinum series listed on page 173.

Isomerism of Complex Salts. Two or more compounds that have identical percentage chemical composition but possess different chemical and physical properties are termed **isomers,** and the phenomenon is called **isomerism.** Isomerism occurs frequently in organic chemistry. For example, two hydrocarbons, *A* and *B*, upon analysis are found to be composed of 92.25 per cent carbon and 7.75 per cent hydrogen. Hence, the simplest formula representing their composition is CH. Molecular-weight determinations give an empirical formula C_2H_2 (acetylene) for *A* and C_6H_6 (benzene) for *B*. Polymerism among inorganic com-

[3] *Op. cit.*, p. 35.

pounds is illustrated by the following reactions: A monomolecular compound, silver cyanide, is formed by the action of H_2SO_4 upon $K[Ag(CN)_2]$ according to the equation

$$K[Ag(CN)_2] + H_2SO_4 \rightarrow AgCN + KHSO_4 + HCN$$

When silver nitrate is added to this same complex salt, a bimolecular polymer is formed:

$$K[Ag(CN)_2] + AgNO_3 \rightarrow Ag[Ag(CN)_2] + KNO_3$$

Polymers of sodium metaphosphate, $NaPO_3$, are $(NaPO_3)_2$, $(NaPO_3)_3$, etc. Similar polymerization phenomena exist among inorganic complex salts, as well as the following types of isomerism: coordination isomerism, hydrate isomerism, and ionization isomerism.

Stereoisomerism of Complex Salts. A large number of compounds of cobalt, chromium, and platinum exhibit the phenomenon of isomerism although no difference in the structure of the two isomers can be identified, either on the basis of electrolytic dissociation or of analytical behavior, as polymerism or any of the other types of isomerism discussed previously. Since a different structure cannot be assigned to them from their chemical behavior, they are said to be structurally identical. Yet it is perfectly evident, from differences in color, that some kind of dissimilarity must exist.

Although in these cases a structurally isomeric formulation is impossible, a difference in the structure of the isomers is conceivable if the arrangement of the individual components of the molecule varies in regard to spatial relations. A difference of this kind, of course, would not be apparent in a formula constructed in the plane of the paper.

If one thinks of a metal ammine compound with the coordination number six, $[Co(NH_3)_6]Cl_3$ for example, as a geometric figure, the simplest supposition is that all six coordinated groups lie in equivalent positions at equal distances from the central atom. The octahedral arrangement fulfills this condition if we consider the central atom to be placed in the center and the other components at the corners of the octahedron. See Fig. 10. The radicals in indirect union, which are split off as ions in solution, need not be taken into consideration. Their conduct as a whole indicates that they have no influence whatsoever on the structure of the nucleus, but that they are linked to the complex in some looser manner, not to be defined more definitely, which permits them great freedom of motion.

This primary, purely theoretical assumption of the octahedral structure for a large class of inorganic complex compounds secures a firm footing from two facts: first, all the phenomena of isomerism hitherto unexplained become reconciled by its help; and second, up to this time no phenomena contrary to it, and necessitating another method of explanation, have been observed. On the other hand, a number of isomeric compounds predicted on the basis of this hypothesis have actually been prepared synthetically.[4]

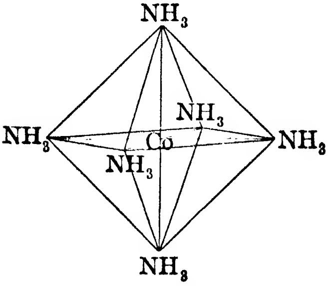

FIG. 10

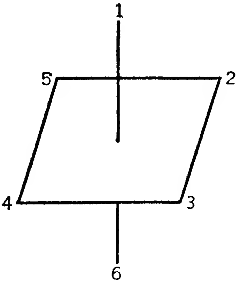

FIG. 11

In order to simplify the writing of space formulas of complex compounds, the symbol of the central atom is omitted and the individual corners of the octahedron are indicated by numbers from 1 to 6 as shown in Fig. 11.

To illustrate the use of this "skeleton octahedral" formula, let us write the space formula for each of the following cobalt ammines:

(1) $[Co(NH_3)_6]$, (2) $[Co(NH_3)_5NO_2]$, (3) $[Co(NH_3)_4(NO_2)_2]$

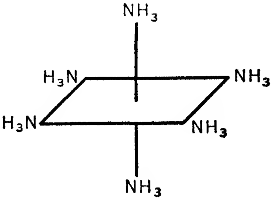

FIG. 12

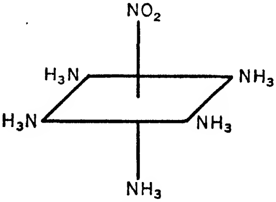

FIG. 13

Formula (1) is represented by Fig. 12. For formula (2) the position of the NO_2 radical is immaterial (Fig. 13), but for formula (3) two configurations are possible (Fig. 14), and two salts of

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[4] Schwarz-Bass, *op. cit.*, pp. 48–49.

the formula $[Co(NH_3)_4(NO_2)_2]$ actually exist—a brown form (called the flavo-salt), and a yellow form (the croceo-salt). In the brown salt, the NO_2 radicals stand in neighboring positions, termed **cis**-positions; in the other, the NO_2 groups are separated or in the **trans**-positions. The **cis**- and **trans**-positions are also referred to as edge (1, 2) and axial (1, 6) substitution. Perhaps you have asked yourself the question: Why was the **cis**-configuration assigned to the brown flavo-salt and the **trans**-configuration given the yellow croceo-salt? The answer is: By studying certain reactions involved in the preparation of the two salts. For details of the proof, the student is referred to Schwarz-Bass, "The Chemistry of the Inorganic Complex Compounds," page 59.

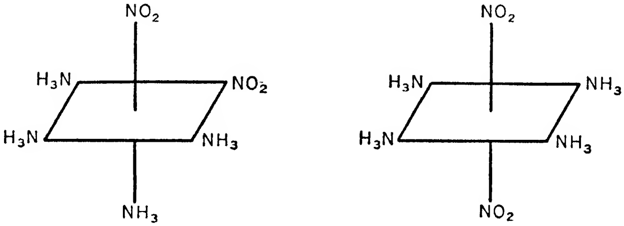
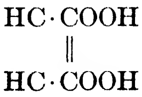


FIG. 14

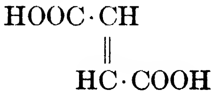
Cis-trans isomerism was discovered first among organic compounds; for example, fumaric and maleic acids both have the formula HOOC·CH : CH·COOH. A molecule of this composition may have either of the following spatial configurations:



$$\begin{array}{c}\mathrm{HC\cdot COOH}\\ \| \\ \mathrm{HC\cdot COOH}\end{array}$$

Cis-form
(Maleic acid)

and



$$\begin{array}{r}\mathrm{HOOC\cdot CH}\\ \|\\ \mathrm{HC\cdot COOH}\end{array}$$

Trans-form
(Fumaric acid)

The decision as to which acid has the **cis**-form and which the **trans**- is based upon a study of their chemical properties. The student is referred to a textbook on organic chemistry for this proof.[5]

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[5] See Conant, "The Chemistry of Organic Compounds," p. 291, the Macmillan Co., New York, 1933; Bernthsen (revised by Sudborough), "A Textbook of Organic Chemistry," p. 255, D. Van Nostrand Co., New York, 1931.

COMPLEX-ION EQUILIBRIA

Many separations and identifications in qualitative analysis depend upon the formation of complex ions. The following are the more important:

1. Complex metal-ammonia ions—e.g.,

$$[Ag(NH_3)_2]^+,\ [Cu(NH_3)_4]^{++},\ [Cd(NH_3)_4]^{++}$$

$$[Co(NH_3)_4]^{++},\ [Ni(NH_3)_4]^{++},\ \text{and}\ [Zn(NH_3)_4]^{++}$$

2. Complex metal-sulfide ions—e.g.,

$$AsS_3^{\equiv},\ AsS_4^{\equiv},\ SbS_3^{\equiv},\ SbS_4^{\equiv},\ SnS_3^{=},\ HgS_2^{=}$$

3. Complex metal-cyanide ions—e.g.,

$$[Ag(CN)_2]^-,\ [Ag(CN)_3]^{=},\ [Au(CN)_2]^-$$

$$[Cd(CN)_4]^{=},\ [Cu(CN)_3]^{=},\ [Hg(CN)_4]^{=},\ [Ni(CN)_4]^{=}$$

$$[Zn(CN)_4]^{=},\ [Co(CN)_6]^{\equiv},\ [Fe(CN)_6]^{\equiv},\ \text{and}\ [Fe(CN)_6]^{\substack{=\\=}}$$

4. Complex metal-halide ions—e.g.,

$$[AuCl_4]^-,\ [HgCl_3]^-,\ [HgCl_4]^{=},\ [HgBr_4]^{=}$$

$$[HgI_4]^{=},\ [AgCl_3]^{=},\ [PbCl_4]^{=},\ [PtCl_6]^{=},\ \text{and}\ [SnCl_6]^{=}$$

5. Complex metal-thiocyanate ions—e.g.,

$$[Hg(CNS)_4]^{=}\ \text{and}\ [Fe(CNS)_6]^{\equiv}$$

6. Complex metal-organic ions—e.g., oxalate complexes, tartrate complexes, and citrate complexes. The presence of nonvolatile organic matter containing alcohol (OH) groups, such as tartrate, citrate, glycerin, sugar, and starch, prevents the precipitation of $Al(OH)_3$, $Cr(OH)_3$, and $Fe(OH)_3$ by NH_4OH, Na_2CO_3, and $(NH_4)_2S$. This is due to the formation of stable complex ions with the metals, in which the latter replace the H in the alcohol groups (OH) and thus appear in the complex anion. Organic substances such as gelatin, albumen, starch, casein, and glue also interfere with the precipitation of the trivalent metal hydroxides since they are protective colloids. Hence it is necessary to destroy or remove all organic matter before separating and testing for aluminum, chromium, and iron.

Case 28. Calculations involving complex-ion equilibria.

In problems of this type the equilibrium constant is called an instability or complex dissociation constant. The values of a few instability constants are given in Table IX.

TABLE IX

INSTABILITY CONSTANTS

Complex Ion	$K_{\text{(instab.)}}$	Complex Ion	$K_{\text{(instab.)}}$
$Ag(NH_3)_2{}^+$	6.8×10^{-8}	$Hg(CNS)_4{}^{=}$	1×10^{-22}
$Cd(NH_3)_4{}^{++}$	1×10^{-7}	$Ag(S_2O_3)_2{}^{\equiv}$	1×10^{-13}
$Zn(NH_3)_4{}^{++}$	2.6×10^{-10}	$HgS_2{}^{=}$	1×10^{-53}
$Ag(CN)_2{}^-$	1×10^{-21}	$HgCl_4{}^{=}$	6×10^{-17}
$Cu(CN)_3{}^{=}$	5×10^{-28}	$HgBr_4{}^{=}$	2.2×10^{-22}
$Cd(CN)_4{}^{=}$	1.4×10^{-17}	$HgI_4{}^{=}$	5×10^{-32}
$Hg(CN)_4{}^{=}$	4×10^{-42}		

Example 1. A 0.01 *M* solution of silver ammonia complex ions, $[Ag(NH_3)_2]^+$, contains 5.6×10^{-4} gram-ion of Ag^+ ions per liter. Calculate the instability constant of the complex ion.

Silver ammonia complex-ion dissociates as follows:

$$Ag(NH_3)_2{}^+ \rightleftharpoons Ag^+ + 2NH_3$$

Applying the law of chemical equilibrium,

$$\frac{C_{Ag^+} \times C^2_{NH_3}}{C_{Ag(NH_3)_2{}^+}} = K_{\text{(instab)}}$$

$C_{Ag^+} = 5.6 \times 10^{-4}$ and $C_{NH_3} = 1.1 \times 10^{-3}$, and the solution is 0.01 *M* with respect to the complex ion. Substituting these values in the equilibrium equation, we get

$$\frac{5.6 \times 10^{-4} \times (1.1 \times 10^{-3})^2}{0.01} = 6.8 \times 10^{-8}$$

Example 2. Calculate the Ag^+ ion and CN^- ion concentrations in a 0.1 *M* solution of $K[Ag(CN)_2]$. $K_{\text{(instab.)}}$ of $Ag(CN)_2{}^-$ is 1×10^{-21}.

The ionization of the silver cyanide complex ion is as follows:

$$Ag(CN_2)^- \rightleftharpoons Ag^+ + 2CN^-$$

The equilibrium equation is

$$\frac{C_{Ag^+} \times C^2_{CN^-}}{C_{Ag(CN)_2{}^-}} = 1 \times 10^{-21}$$

Let $x = Ag^+$ ion concentration and $2x = CN^-$ ion concentration. Substituting in the equilibrium equation,

$$\begin{aligned}\frac{x \times (2x)^2}{0.1} &= 1 \times 10^{-21}\\ 4x^3 &= 1 \times 10^{-22}\\ x^3 &= 25 \times 10^{-24}\\ x &= 2.9 \times 10^{-8}\end{aligned}$$

Therefore, the concentration of Ag^+ ion is 2.9×10^{-8} gram-ion per liter, and the concentration of the CN^- ion is 5.8×10^{-8} gram-ion per liter.

Example 3. A 0.05 *M* solution of Cu_2Cl_2 is treated with KCN and the reaction is expressed by the equation:

$$Cu_2Cl_2 + 6KCN \rightleftharpoons 2K_2Cu(CN)_3 + 2KCl$$

What are the concentrations of the Cu^+ ions and CN^- ions in the solution thus formed? $K_{(\text{instab.})}$ for $Cu(CN)_3^{=} = 5 \times 10^{-28}$.

Since 1 mol of Cu_2Cl_2 is equivalent to 2 mols of $K_2Cu(CN)_3$, the concentration of the $Cu(CN)_3^{=}$ complex ion will be 0.1 *M*. The complex ion dissociates as follows:

$$Cu(CN)_3^{=} \rightleftharpoons Cu^+ + 3CN^-$$

Let $x = C_{Cu^+}$ and $3x = C_{CN^-}$. Substituting the concentration values in the equilibrium ratio, we get

$$\begin{aligned}\frac{x \times (3x)^3}{0.1} &= 5 \times 10^{-28}\\ 27x^4 &= 5 \times 10^{-29}\\ x^4 &= 0.19 \times 10^{-29} = 190 \times 10^{-32}\\ x &= 3.7 \quad \times 10^{-8}\end{aligned}$$

Therefore, the concentration of Cu^+ ion is 3.7×10^{-8}, and that of CN^- ion is 1.1×10^{-7} gram-ion per liter.

Case 29. The application of the common-ion effect to complex-ion equilibria.

Many complex ions are extremely stable, that is, they ionize only to a very small degree. Hence, the effect of adding a common ion or common constituent may be calculated in the same way as for weak electrolytes.

Example. The concentration of Ag^+ ion in a solution containing 0.01 mol of $Ag(NH_3)_2^+$ per liter is 5.6×10^{-4} gram-ion. If the NH_3 concentration is increased to 0.05 *M*, what will be the concentration of Ag^+ ion? Note the analogy with the common-ion effect. The equilibrium equation for $Ag(NH_3)_2^+$ complex ion is

$$\frac{C_{Ag^+} \times C^2_{NH_3}}{C_{Ag(NH_3)_2^+}} = 6.8 \times 10^{-8}$$

Let x = concentration of Ag^+ ion. Then

$$\frac{x \times (0.05)^2}{0.01} = 6.8 \times 10^{-8}$$

$$0.0025x = 6.8 \times 10^{-10}$$

$$x = 2.7 \times 10^{-7} \text{ gram-ion per liter.}$$

Hence, the Ag^+ ion concentration will be reduced from 5.6×10^{-4} to 2.7×10^{-7} gram-ion per liter, by increasing the NH_3 concentration to 0.05 M.

PROBLEMS

1. When NH_4OH is added to solid AgCl, the latter dissolves owing to the formation of the soluble complex salt, $Ag(NH_3)_2Cl$. (*a*) What is the Ag^+ ion concentration in a 0.1 M $Ag(NH_3)_2Cl$ solution? (Assume complete ionization of the $Ag(NH_3)_2Cl$.) The equilibrium expression for the complex ion is

$$\frac{C_{Ag^+} \times C^2_{NH_3}}{C_{Ag(NH_3)_2^+}} = 6.8 \times 10^{-8}$$

(*b*) What is the concentration of NH_3?

Ans. (*a*) 1.2×10^{-3} gram-ion per l.
(*b*) 2.4×10^{-3} gram-mol per l.

2. Calculate the concentration of (*a*) Ag^+ ion and (*b*) CN^- ion in a 0.1 M solution of $KAg(CN)_2$, the complex salt being 85 per cent ionized.

$$\frac{C_{Ag^+} \times C^2_{CN^-}}{C_{Ag(CN)_2}} = 1 \times 10^{-21}$$

Ans. (*a*) 2.8×10^{-8} gram-ion per l.
(*b*) 5.6×10^{-8} gram-ion per l.

3. The Cd^{++} ion concentration in a 0.1 M $Cd(CN)_4^{=}$ ion solution is 8.9×10^{-6} gram-ion per liter. Calculate the instability constant, or complex dissociation constant, of $Cd(CN)_4^{=}$ ion.

Ans. 1.4×10^{-17}.

4. In a 0.1 M $K_2Cu(CN)_3$ solution the CN^- ion concentration is 1.1×10^{-7} gram-ion per liter. What is the instability constant of $Cu(CN)_3^{=}$ ion?

Ans. 4.9×10^{-28}.

5. In a solution containing 0.01 gram-mol of $Ag(NH_3)_2^+$ ion per liter, the NH_3 concentration is increased to 0.10 gram-mol. (*a*) Calculate the Ag^+ ion concentration present before the NH_3 concentration was increased and after the increase. (*b*) What was the approximate decrease in Ag^+ ion concentration resulting from increasing the NH_3 concentration to 0.1 M?

Ans. (*a*) 5.5×10^{-4}, 6.8×10^{-8}.
(*b*) Ten-thousand fold decrease (approx.)

6. (*a*) Calculate the concentration of Cu^+ ion and CN^- ion, respectively,

in a solution which is 0.01 M in $Cu(CN)_3^-$ ion. (*b*) If the CN^- ion concentration is increased to 0.10 M, what will be the Cu^+ ion concentration?

Ans. (*a*) 2.1×10^{-8}, 6.3×10^{-8}.
(*b*) 5×10^{-27}.

Case 30. Dissolving a precipitate by forming a complex ion. (Other methods of dissolving precipitates are listed on page158.)

Example 1. How many milligrams of sodium sulfide, Na_2S, are required to dissolve 500 mg. of mercuric sulfide?

The reaction is represented by the following equation:

$$\begin{array}{lccccc} \text{Mol. wt.} = & 232.67 & & 78.05 & & \\ & HgS & + & Na_2S & \rightarrow & Na_2HgS_2 \\ & 500 & & x & & \end{array}$$

Hence,

$$\frac{232.67}{500} = \frac{78.05}{x}$$

$$x = 168 \text{ mg. } Na_2S$$

Example 2. How many milliliters of concentrated ammonium hydroxide[6] (sp. gr. 0.900 and containing 28.33 per cent NH_3 by weight) are required to dissolve 0.25 g. of silver chloride?

The silver chloride dissolves according to the reaction

$$\begin{array}{lccccc} \text{Mol. wt.} = & 143.34 & & (2 \times 17.03) & & \\ & AgCl & + & 2NH_3 & \rightarrow & Ag(NH_3)_2Cl \\ & 0.25 & & x & & \end{array}$$

Hence,

$$\frac{143.34}{0.25} = \frac{34.06}{x}$$

$$x = 0.0593 \text{ g. } NH_3$$

Each milliliter of concentrated NH_4OH contains

$$1 \times 0.900 \times 0.2833 = 0.255 \text{ g. } NH_3$$

$$\therefore \quad \frac{0.0593}{0.255} = 0.23 \text{ ml. conc. } NH_4OH$$

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[6] Ammonium hydroxide is an aqueous solution of ammonia gas. It contains H_2O, NH_3, NH_4OH, NH_4^+, and OH^-. Most of the ammonia is present as dissolved NH_3. Of the small amount of NH_4OH present, only a small fraction is ionized into NH_4^+ and OH^- ions.

PROBLEMS

1. (*a*) What weight of NH_3 is required to dissolve 0.5 g. of AgCl? (*b*) What volume of concentrated NH_4OH (sp. gr. 0.900, 28.33 per cent NH_3 by weight) would be required?

Ans. (*a*) 0.12 g.
(*b*) 0.47 ml.

2. Calculate the milliliters of 1 *M* KCN required to dissolve 0.1 gram-mol of AgCl.

Ans. 200 ml.

3. How many milliliters of concentrated NH_4OH (sp. gr. 0.900, 28.33 per cent NH_3 by weight) must be used to dissolve 5 g. of $Cu(OH)_2$? $Cu(OH)_2 + 4NH_3 \rightarrow Cu(NH_3)_4^{++} + 2OH^-$.

Ans. 13.7 ml.

4. Calculate the weight of Na_2S required to dissolve 100 mg. of each of the following sulfides: (*a*) HgS, (*b*) As_2S_5, (*c*) Sb_2S_5, and (*d*) SnS_2. $HgS + Na_2S \rightarrow Na_2HgS_2$; $As_2S_5 + 3Na_2S \rightarrow 2Na_3AsS_4$.

Ans. (*a*) 33.5 mg. (*c*) 58.0 mg.
(*b*) 75.5 mg. (*d*) 42.6 mg.

5. How many milligrams of NH_3 are required to dissolve 50 mg. of $Ni(OH)_2$?

Ans. 36.7 mg.

6. (*a*) How much NaCN must be used to dissolve 0.25 g. of $Cd(OH)_2$? (*b*) What volume of 1 *M* NaCN can be prepared from the weight of NaCN used in (*a*)?

Ans. (*a*) 0.34 g.
(*b*) 6.9 ml.

7. (*a*) Write the equation showing the ionization of tartaric acid, $H_2C_4H_4O_6$, in aqueous solution. (*b*) Show how the tartrate undergoes further ionization on making its aqueous solution alkaline. (*c*) Show how the complex tartrate ion formed in (*b*) unites with certain metallic ions (e.g., Cu^{++}, Al^{+++}, Cr^{+++}, Fe^{+++}), yielding complex metal-tartrate ions. Use graphic (structural) formulas in writing the equations. These soluble complex metal-tartrates are very stable, and hence only metallic compounds of extremely low solubility can be precipitated from their solutions.

8. A large class of organic compounds, such as citric acid, the sugars, glycerin, etc, which contain alcohol groups form complex metal-organic ions similar to the complex metal-tartrate ions. (*a*) Show by means of equations, using structural formulas, the ionization of citric acid, $COOH \cdot C(OH)(COOH) \cdot CH_2 \cdot COOH$, and the mechanism of the formation of complex cupricitrate ion.

CHAPTER XVIII

THE *p*H SCALE. NEUTRALIZATION AND HYDROLYSIS

The Ionization Equilibrium of Water. According to the electrolytic dissociation theory, hydrogen ions and hydroxyl ions are present in water and in all liquids which contain water. When the total number of hydrogen ions is exactly equal to the total number of hydroxyl ions per given volume, the solution is neutral. When the hydrogen ions are in excess, the solution is acid; when the hydroxyl ions are in excess, the solution is alkaline. It has already been pointed out that the H^+ ion is characteristic of all acid solutions and that it is this ion which is responsible for the various properties acids possess in common. As the H^+ ion concentration increases, the acidity increases. Hence, strong acids are those which are highly dissociated (ionized) in solution, or yield a large number of H^+ ions. Conversely, weak acids are those which are only slightly dissociated in solution. Similarly, strong bases are those which are highly dissociated in solution, or produce a large number of OH^- ions; and weak bases yield only a relatively few OH^- ions upon ionizing in solution. The **strength** of an acid or a base must not be confused with its neutralizing power. For example, hydrochloric acid is a strong acid and acetic acid is a weak acid. But in titration, equal volumes of these acids of the same normality, i.e., same number of gram-ions of H^+ ion per liter, will neutralize exactly the same amount of any base. Twenty-five milliliters of 0.1 *N* HCl and 25 ml. of 0.1 *N* CH_3COOH will each require 25 ml. of 0.1 *N* KOH for neutralization. However, the number of H^+ ions in the hydrochloric acid solution is almost 70 times as great as the number of H^+ ions in the acetic acid solution. Hence, the **concentration** of the H^+ ion cannot be determined by simple titration. The titration gives the **total acidity** or **total available** H^+ ions in the acid solution. The H^+ ion concentration requires a special determination, and the methods will be discussed subsequently. Likewise, the titration of a base gives the **total**

alkalinity or **total available** OH^- ions in the basic solution. Methods for determining OH^- ion concentrations are the same as those used for the H^+ ion determination.

Experiment shows that the purest water yet prepared will conduct the electric current to a very slight degree. Hence, water must contain a very low concentration of H^+ ions and OH^- ions, which are the current carriers. Kohlrausch found that pure water has a molar conductivity of 5.0×10^{-5} reciprocal ohm at 25° C. According to Kohlrausch's law (see page 246), the molar conductivity, Λ, of an electrolyte is equal to the sum of its ionic conductivities. Hence, if a liter of water at 25° contained 1 gram-mol (18 g.) of completely ionized water, its molar conductivity should equal the sum of the conductivities of the H^+ ion and OH^- ion, $313 + 174 = 487$. But, since by actual measurement the molar conductivity of water at 25° is only 5×10^{-5}, it follows that the extent or degree of ionization of water is $\frac{5.0 \times 10^{-5}}{487} = 1 \times 10^{-7}$ (approximately). The value for the fraction of a mol (18 g.) of water ionized in 1 liter at 25° has been determined by about six different methods and all give substantially 1×10^{-7} mol per liter.

The ionization of water may be expressed by the following equation:

$$H_2O \rightleftharpoons H^+ + OH^-$$

Applying the law of chemical equilibrium, we have the following relationship for the undissociated water molecules in equilibrium with H^+ ions and OH^- ions:

$$\frac{C_{H^+} \times C_{OH^-}}{C_{H_2O}} = K \qquad (1)$$

where K is the equilibrium constant of water. But since the concentration of undissociated water, C_{H_2O}, is relatively extremely large (almost unity), it can be considered a constant, and hence equation (1) becomes

$$C_{H^+} \times C_{OH^-} = K \times C_{H_2O} = K_w$$

K_w being called the ion-product constant of water. It should be noted that K_w is a "modified" ionization constant, just as $C^2_{H^+} \times C_{S^=} = K_{(H_2S)}$ expresses the relation between H^+ ions and $S^=$ ions in equilibrium with H_2S.

The *p*H Scale or the Hydrogen-Ion Exponent Scale. If the ionization of water at constant temperature remained constant, irrespective of the presence or absence of dissolved substances, then its ion-product, K_w, should serve as a basis for a scale of acidity or alkalinity. Unfortunately this is not the situation, as Harned[1] has shown that the value of K_w in salt solutions is not constant. For salts such as NaCl, K_w increases until at a concentration 0.5 M it is about twice the value for pure water. At higher salt concentrations, K_w decreases. However, for all **dilute** aqueous solutions the value of K_w is approximately constant at constant temperature and the following relations exist: $C_{\text{H}^+} = \dfrac{K_w}{C_{\text{OH}^-}}$, and $C_{\text{OH}^-} = \dfrac{K_w}{C_{\text{H}^+}}$. In other words, the reaction of any **dilute** aqueous solution (acid, alkaline, or neutral) may be expressed in terms of either the H^+ ion or the OH^- ion concentration. In pure water, $C_{\text{H}^+} = C_{\text{OH}^-} = \sqrt{10^{-14}} = 10^{-7}$ gram-ion per liter at 25°. Hence, we may write an H^+ ion or an OH^- ion scale as follows:

	ACID SOLUTIONS		NEUTRAL SOLUTION	ALKALINE SOLUTIONS	
Normality	1	0.1	0.01....↑...... 0.01	0.1	1
C_{H^+}	10^0	10^{-1}	10^{-2}.....10^{-7}....10^{-12}	10^{-13}	10^{-14}
C_{OH^-}	10^{-14}	10^{-13}	10^{-12}....10^{-7}....10^{-2}	10^{-1}	10^{-0}

Sørensen[2] recognized the inconvenience of such a scale and proposed a simpler one in which the numerical values of the negative exponents of hydrogen-ion concentration, C_{H^+}, are the basis of a scale. He suggested the symbol $p_{\overset{+}{\text{H}}}$,[3] but Clark proposed using the symbol *p*H as a matter of typographical convenience. Since the *p*H value is the logarithm of the reciprocal of the hydrogen-ion concentration, C_{H^+}, the general relation may be expressed as follows:

$$p\text{H} = \log \frac{1}{C_{\text{H}^+}} = -\log C_{\text{H}^+}, \text{ or } C_{\text{H}^+} = 10^{-p\text{H}}$$

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[1] *Trans. Am. Electrochem. Soc.*, **51**, 571 (1927).

[2] Sørensen, *Biochem. Z.*, **21**, 131 (1909).

[3] The *p* stands for the French word "puissance," meaning *power* (mathematical). The corresponding German word is "Potenz."

Similarly, we may express the relation of pOH to C_{OH^-}:

$$p\mathrm{OH} = \log \frac{1}{C_{\mathrm{OH}^-}} = -\log C_{\mathrm{OH}^-}, \text{ or } C_{\mathrm{OH}} = 10^{-p\mathrm{OH}}$$

From the above relations we may write pH and pOH scales which correspond to the H^+ ion concentration.

Scale				Acid			←	Neutral	→			Alkaline			
C_{H^+}	10^0	10^{-1}	10^{-2}	10^{-3}	10^{-4}	10^{-5}	10^{-6}	10^{-7}	10^{-8}	10^{-9}	10^{-10}	10^{-11}	10^{-12}	10^{-13}	10^{-14}
pH	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14
pOH	14	13	12	11	10	9	8	7	6	5	4	3	2	1	0

An inspection of the above table shows that pH values below 7 denote acidity, the degree of acidity increasing as the numbers **decrease.** For example, if a small amount of hydrochloric acid is added to pure water which has an H^+ ion concentration of 10^{-7} or a pH of 7, the acid will ionize into H^+ ions and Cl^- ions. The total number of H^+ ions in the solution will then be greater than 10^{-7} and hence the solution will be acid. Suppose the H^+ ion concentration is found to be 0.000001 N. The pH will be the log of 1/0.000001 or 1,000,000, which is 6. Likewise, a 0.00001 N H^+ ion solution has a pH of 5, and so on up to an acidity of 1 N or pH 0. It should be remembered that the pH scale is a logarithmic scale; i.e., each pH unit represents a tenfold difference in H^+ ion concentration. For example, a solution having a pH of 6 has ten times as many H^+ ions as one with a pH of 7. A solution with a pH of 5 has one hundred times as many H^+ ions as a solution of pH 7.

An inspection of the ion-product equation for water, $C_{H^+} \times C_{\mathrm{OH}^-} = K_w$, shows that as the H^+ ion concentration increases the OH^- ion concentration must decrease correspondingly, and *vice versa.* However, even a strongly alkaline solution contains some H^+ ions, and so for the sake of simplicity both acidity and alkalinity are expressed in terms of pH values. This is merely a matter of convention, of course, for the pOH scale could be used equally well. In using the pH scale, simply remember that all solutions with a pH less than 7 are acid; all with a pH greater than 7 are alkaline. Remember further that decreasing pH values means **increasing** acidity, and increasing pH values means increasing alkalinity or **decreasing** acidity. Also, a solution with *p*H 8 contains ten times as many OH^- ions as one with *p*H 7, and so on.

From the foregoing discussion it will be seen that the *p*H scale is a definite and accurate measure of the **degree** of acidity or alkalinity of a solution. The *p*H of a solution can be measured accurately and a definite value recorded, which can be duplicated at any time by the same or different workers. Hence, we are not dependent upon such vague and meaningless terms as "slightly," "moderately," or "strongly" acid or alkaline.

Case 31. Calculation of *p*H Values.

Let us now turn to a consideration of how *p*H values are calculated. Suppose we have a solution of HCl which upon analysis is found to contain 3.65 g. of HCl per liter. This weight of HCl contains 0.1 g. of ionizable H per liter; i.e., the solution is 0.1 *M*. Now, electrical conductivity measurements have shown that 0.1 *M* HCl is 92.0 per cent ionized at 18° C. In other words, 920 molecules of HCl out of every 1000 are dissociated into H^+ and Cl^-, the remaining 80 molecules being undissociated. Hence a liter of 0.1 *M* HCl contains $0.1 \times 0.920 = 0.0920$ gram-ion of H^+ ions.

$$\text{The } p\text{H} = \log \frac{1}{C_{\text{H}^+}} = \log \frac{1}{0.0920} = \log 10.87 = 1.04$$

A 0.1 *M* CH_3COOH solution also contains 0.1 gram-ion of ionizable H per liter, but electrical conductivity measurements show that it is only 1.34 per cent dissociated at 18° C. Hence, the H^+ ion concentration is $0.1 \times 0.0134 = 0.00134$ gram-ion per liter. Therefore the *p*H of 0.1 *M* CH_3COOH is the logarithm of $\frac{1}{0.00134}$ or 746, which is 2.87.

Since the H^+ ion concentration of 0.1 *M* HCl is 0.0920 gram-ion per liter and of 0.1 *M* CH_3COOH is 0.00134 gram-ion per liter, the hydrochloric acid solution contains almost 70 times as many H^+ ions as the acetic acid.

For pure aqueous solutions of alkalies, the *p*H is calculated indirectly by first calculating the OH^- ion concentration, then the *p*OH. The method is precisely the same as that used for calculating *p*H. For example, a 0.1 *M* NaOH solution at 25° C. is 92.9 per cent ionized. Therefore, the OH^- ion concentration is $0.1 \times 0.929 = 0.0929$ gram-ion per liter. Hence, the *p*OH

$= \log \frac{1}{0.0929} = \log 10.76$, which is 1.03. Since $C_{H^+} \times C_{OH^-} = 10^{-14}$, $p\text{H} + p\text{OH} = 14.0$, and, therefore, $p\text{H} = 14.0 - 1.03 = 12.97$.

Before considering *p*H calculations any further, let us consider examples involving only the H^+ ion or the OH^- ion concentration.

Example 1. What is the H^+ ion concentration of 0.1 *M* $HC_2H_3O_2$ which is 1.34 per cent ionized at 18° C.?

Acetic acid ionizes as follows:

$$HC_2H_3O_2 \rightleftharpoons H^+ + C_2H_3O_2^-$$

1.34 per cent of the 0.1 mol of acid is ionized into H^+ ions and $C_2H_3O_2^-$ ions. Hence the H^+ ion concentration is

$$\begin{aligned} 0.1 \times 0.0134 &= 0.00134 \\ &= 1.34 \times 10^{-3} \text{ gram-ion per liter} \end{aligned}$$

Example 2. What is the OH^- ion concentration of 1.0 *M* NH_4OH which at 25° C. is 0.42 per cent dissociated?

Ammonium hydroxide ionizes as follows:

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

0.42 per cent of the 1.0 mol of NH_4OH is ionized into NH_4^+ ions and OH^- ions. Hence the OH^- ion concentration is

$$\begin{aligned} 1.0 \times 0.0042 &= 0.0042 \\ &= 4.2 \times 10^{-3} \text{ gram-ion per liter} \end{aligned}$$

Examples 1 and 2 may also be solved by means of the Ostwald dilution equation (see page 90).

The calculation of *p*H values is illustrated in the following examples:

Example 3. The H^+ ion concentration of a solution is 1×10^{-3} gram-ion per liter. Calculate the *p*H.

$$\begin{aligned} p\text{H} &= \log \frac{1}{C_{H^+}} = \log \frac{1}{1 \times 10^{-3}} \\ &= \log 1 - \log (1 \times 10^{-3}) \\ &= 0 - (-3) \\ &= 3 \end{aligned}$$

When the H^+ ion concentration is expressed in the pure exponential form, the *p*H value is the exponent with its sign changed. For example, $C_{H^+} = 1 \times 10^{-8}$, $p\text{H} = 8$; $C_{H^+} = 1 \times 10^{-4.5}$, $p\text{H} = 4\ 5$.

Example 4. The H^+ ion concentration of a solution is 7.2×10^{-9} gram-ion per liter. What is the pH of the solution?

First convert 7.2×10^{-9} to the pure exponential form.

$$\begin{aligned}
\log (7.2 \times 10^{-9}) &= \log 7.2 + \log 10^{-9} \\
&= 0.8573 + (-9) \\
\therefore \quad \log (7.2 \times 10^{-9}) &= -8.1 \\
7.2 \times 10^{-9} &= 1 \times 10^{-8.1} \\
pH &= \log \frac{1}{C_{H^+}} \\
&= \log \frac{1}{1 \times 10^{-8.1}} \\
&= \log 1 - \log 1 \times 10^{-8.1} \\
&= 0 - (-8.1) \\
&= 8.1
\end{aligned}$$

Note that the interconversion of C_{H^+} values and pH values can be made directly only when the significant value of C_{H^+} is incorporated in the exponential value; i.e., when C_{H^+} is expressed in the pure exponential form. In this form, the pH is the exponent with the sign changed. This follows from the definition of pH and the relationship between exponents and logarithms. Hence, when C_{H^+} is expressed as a mixed number, i.e., partly as the coefficient and partly in the exponent, it must be converted to the pure exponential form before the pH can be obtained directly from the exponent.

Case 32. Calculation of pOH values.

The relation of C_{H^+} to pH and pOH is given on page 187. From this relationship it is evident that the pOH may be obtained by subtracting the pH value from 14. Expressed as an equation for water at room temperature, we have

$$pH + pOH = pK_w = 14$$

Or, the pOH value may be calculated from the OH^- ion concentration in the same way the pH value is calculated from the H^+ ion concentration. The equation for pOH is

$$pOH = \log \frac{1}{C_{OH^-}} = -\log C_{OH^-}$$

Another variation in the method of calculating pOH values is

$$C_{\mathrm{H}^+} \times C_{\mathrm{OH}^-} = K_w = 1 \times 10^{-14} \text{ at } 25^\circ \text{ C.}$$

$$C_{\mathrm{OH}} = \frac{1 \times 10^{-14}}{C_{\mathrm{H}^+}}$$

By substituting the value of C_{H^+} in the equation, C_{OH} may be calculated. When C_{H^+} is expressed in the pure exponential form, then pOH is the C_{OH^-} exponent with the sign changed. For example, the C_{H^+} of a solution is 1×10^{-5} mol per liter. What is its pOH?

$$C_{\mathrm{OH}^-} = \frac{K_w}{C_{\mathrm{H}^+}} = \frac{1 \times 10^{-14}}{1 \times 10^{-5}}$$

$$= 1 \times 10^{-9}$$

$$\therefore\ p\mathrm{OH} = 9$$

In practice, the pOH value is seldom used, the convention being to express acid, alkaline, and neutral solutions in terms of the pH value. The reaction of any aqueous solution at room temperature (about 25° C.) is defined by the following expressions:

$p\mathrm{H} < 7 < p\mathrm{OH}$ Acid solution
$p\mathrm{H} = 7 = p\mathrm{OH}$ Neutral solution
$p\mathrm{H} > 7 > p\mathrm{OH}$ Alkaline solution

In Table X is shown the relationship between the **total** acidity or basicity, and the pH values of a few common acids and bases. The pH values are for 0.1 M solutions and are rounded off to the nearest 0.1, as this is sufficiently accurate for most purposes.

TABLE X

APPROXIMATE pH VALUES OF SOME COMMON ACIDS AND BASES *

Acids—0.1 M	pH Value	Bases—0.1 M	pH Value
Hydrochloric acid	1.0	Sodium bicarbonate	8.4
Sulfuric acid	1.2	Borax	9.2
Phosphoric acid	1.5	Ammonium hydroxide	11.1
Sulfurous acid	1.5	Sodium carbonate	11.6
Acetic acid	2.9	Trisodium phosphate	12.0
Alum	3.2	Sodium metasilicate	12.2
Carbonic acid	3.8	Calcium hydroxide	12.3
Boric acid	5.2	Sodium hydroxide	13.0

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* From "The A B C of pH Control," sixth edition, LaMotte Chemical Products Co., Baltimore, Md., 1930.

MAKING HYDROGEN-ION DETERMINATIONS

There are two methods of making hydrogen-ion or *p*H determinations: (1) the colorimetric method, and (2) the potentiometric method. The colorimetric method, which is simpler and quicker, is based on the fact that various indicators (organic dyestuffs) undergo definite color changes when they are acted upon by solutions of different acidities or alkalinities. The potentiometric method depends upon a measurement of the electromotive force produced in an electrolytic cell. After thus determining the H^+ ion concentration, or *p*H, of a series of buffer solutions over the range of *p*H 0 to 14, it is then a simple matter to select a group of indicators which will cover the entire *p*H range. Such a list is shown in Table XI.

TABLE XI *

Name	*p*H Range	Color Change
Acid cresol red	0.2–1 8	Red–yellow
Meta cresol purple	1.2–2.8	Red–yellow
LaMotte yellow	2.6–4.2	Red–yellow
Bromphenol blue	3.0–4.6	Yellow–blue
Bromcresol green	3.8–5.4	Yellow–blue
Methyl red	4.4–6.0	Red–yellow
Chlorphenol red	5.2–6.8	Yellow–red
Bromthymol blue	6.0–7.6	Yellow-blue
Phenol red	6.8–8.4	Yellow–red
Cresol red	7.2–8.8	Yellow-red
Thymol blue	8.0–9.6	Yellow–blue
LaMotte purple	9.6–11.2	Purple–red
LaMotte sulfo orange	11.0–12.6	Pale yellow–deep orange
LaMotte violet	12.0–13.6	Red–blue

* From "The A B C of *p*H Control."

Each indicator covers a definite and narrow *p*H range, which is quickly determined, once for all, by simply adding a few drops of indicator solution to a measured volume of each of the standard buffer solutions. The colorimetric method is accurate to about 0.1 *p*H unit; the potentiometric method is accurate to 0.01 *p*H unit when proper precautions are taken. A brief description of each method will now be given.

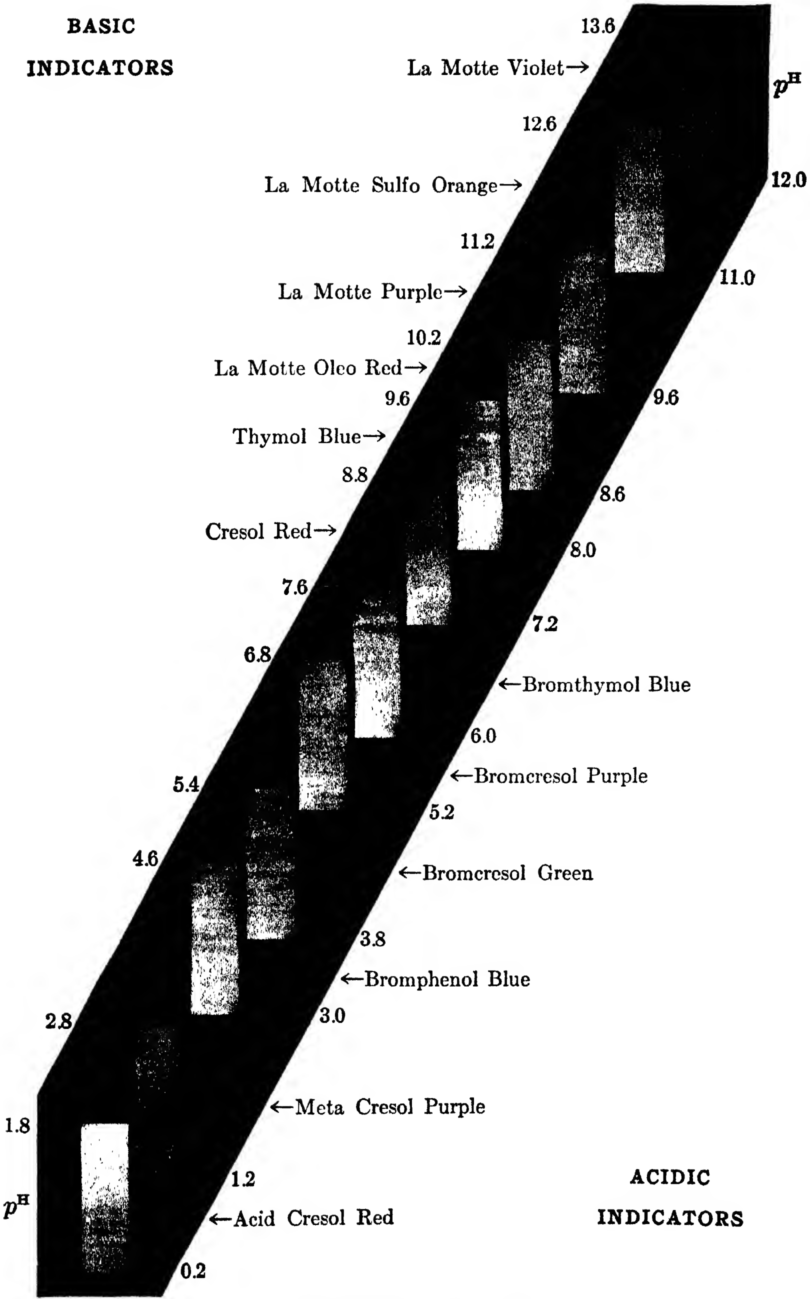

FIG. 15.—Indicator Color Chart

By permission from Rice and Cortelyou, "Popoff's Quantitative Analysis," third edition.

The Colorimetric Method of pH Determination. Before describing the technique of making pH determinations colorimetrically, let us consider the color change of acid-base indicators. These indicators behave like weak acids or weak bases, the dissociated and undissociated forms of which differ both in color and constitution. Hence, it is possible to interpret the behavior of indicators quantitatively by applying the law of chemical equilibrium. Consider an indicator, HI, whose undissociated form has acid properties. Its dissociation is represented by the same equation as that for all weak acids:

$$\underset{\substack{\text{Acid form}\\\text{(has acid color)}}}{\text{HI}} \rightleftharpoons \text{H}^+ + \underset{\substack{\text{Basic form}\\\text{(has basic color)}}}{\text{I}^-}$$

The equilibrium is governed by:

$$\frac{C_{\text{H}^+} \times C_{\text{I}^-}}{C_{\text{HI}}} = K_{\text{I}} \tag{1}$$

where K_{I} is the ionization constant of the indicator, often called the **indicator constant.** The color of the indicator in the solution is determined by the ratio C_{I^-} to C_{HI}:

$$\frac{C_{\text{I}^-}}{C_{\text{HI}}} = \frac{K_{\text{I}}}{C_{\text{H}^+}} \tag{2}$$

Hence, at any hydrogen-ion concentration both forms of the indicator are present. The color change takes place gradually with changes in hydrogen-ion concentration. If an indicator added to different solutions assumes the same transition shade, the solutions are assumed to have the same pH.[4] In other words, the same color means the same ratio of acid to basic form (C_{HI}: C_{I^-}):

$$C_{\text{H}^+} = \frac{C_{\text{HI}}}{C_{\text{I}^-}} K_{\text{I}} \tag{3}$$

or

$$pH = \log \frac{1}{C_{\text{H}^+}}$$

$$= \log \frac{C_{\text{I}^-}}{C_{\text{HI}}} + pK_{\text{I}} \tag{4}$$

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[4] For a discussion of sources of error in the colorimetric method, see Kolthoff, "The Colorimetric and Potentiometric Determination of pH," p. 52, John Wiley & Sons, New York, 1931.

where pK_I is the negative logarithm of the ionization constant of the indicator. The value of *p*H at the 50 per cent transformation is called the indicator's *pK* value.

If the approximate *p*H of a given solution is known, then a suitable indicator solution may be selected and 0.5 ml. of it added to 10 ml. of the solution whose *p*H is to be measured. After mixing, the resulting colored solution is matched in a block comparator, Fig. 16, with a series of standard buffer solutions prepared so that they differ in *p*H by 0.2 unit and to 10 ml. of each of which has been added 0.5 ml. of the indicator solution. Matching, as a rule, may easily be made to 0.1 *p*H unit. If an exact match is obtained, the *p*H of the solution is read off directly from the standard which it matches. If the color is between two standards, the *p*H value is taken as the average of the two standards. For example, if the standards have *p*H values of 6.4 and 6.6, the *p*H of the solution is taken to be 6.5.

Courtesy of LaMotte Chemical Products Co., Baltimore

FIG. 16.—Block Comparator

If the approximate *p*H of the solution is not known, then it is necessary first to make a rough determination. This is done by adding 0.5 ml. of bromthymol blue (*p*H range 6.0–7.6) to 10 ml. of the sample. Since this indicator covers the neutral point, *p*H 7.0, it is possible to determine whether the solution is acid, neutral, or alkaline. If the solution is either very acid or very alkaline, another indicator must be tried, the exact *p*H finally being determined as outlined in the preceding paragraph. If the pH is within the range of 6.0 to 7.6, then an exact match in color is made as described in the preceding paragraph.

The special arrangement of the tubes (Fig. 17) in the comparator block eliminates any effects of color or turbidity in the original sample, since the observer is looking through exactly the same materials in each pair of tubes. That is, tube-pairs *A* and *D*, *B* and *E*, *C* and *F* each contain the color or turbidity present in the sample *G*, indicator solution *I*, and distilled water *W*. The only difference in the three tube-pairs is in *B* and *E*, in which the indicator solution has been added to the sample *B*, instead of to the distilled-water tube *E* which is placed in front of it. The final combination, however, is the same in all three pairs. Hence, when the proper color standards have been inserted, tubes *D* and *F* for instance, an exact match can be obtained.

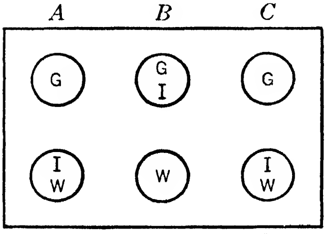

FIG. 17

A further aid in making accurate measurements is obtained by placing a piece of etched glass over the slots on one side of the comparator block and then holding the block so the etched glass is on the side facing the source of light. In this way the reflection of outside objects in the tubes is eliminated.

All pH measurements should be made at room temperature, that is, between 20° and 30° C. If this is not possible, care should be taken that all measurements on the same material be made at the same temperature.

The Potentiometric Method of pH Determination. As has already been stated, this method is based upon measuring the electromotive force produced in an electrolytic cell. Such a cell is made up of two so-called " half-cells," one of which is a hydrogen electrode which dips into a 1 *M* H^+ ion solution, and the other a hydrogen electrode which dips into the solution of unknown H^+ ion concentration. The hydrogen electrode consists of platinum black (very finely divided platinum) deposited upon an inert metal, such as platinum, gold, or iridium, and then saturated with hydrogen gas by slowly bubbling the latter through the cell at 1 atmosphere pressure. The two half-cells are connected by a

U-tube filled with a suitable conducting liquid, say 1 M KCl solution, and the electrodes are attached to a potentiometer. Upon closing the circuit, the potential difference, E, is read in millivolts on the potentiometer. This value, E, is related to the concentrations in the two half-cells by the Nernst equation.

$$E = 0.059 \log \frac{1}{C_{\mathrm{H}^+}}$$

in which 0.059 is a constant, 1 is the H^+ ion concentration in the 1 M acid solution, and C_{H^+} is the H^+ ion concentration in the sample solution. Hence, by measuring E, the equation can be solved for C_{H^+}.

$$\frac{E}{0.059} = \log \frac{1}{C_{\mathrm{H}^+}} = p\mathrm{H}$$

The potentiometric method of measuring pH is really the fundamental method upon which the colorimetric method depends. However, once the pH values of a series of buffer solutions are established by the potentiometric method, then it is possible to use these as standards for comparisons by the colorimetric method. Such series of standard buffer solutions are now available on the market or can be easily and readily prepared from pure buffer salts.

Buffer Action. It has already been pointed out (page 90) that the effect of a common ion on the equilibrium of a weak acid or base is the basis of *buffer action,* which is described by Clark as the resistance exhibited by a solution to change in pH through the addition or loss of acid or alkali. Let us consider the reaction in a mixture of a weak acid with its salt. The dissociation of a weak acid into its ions is governed by the magnitude of the ionization constant:

$$\frac{C_{\mathrm{H}^+} \times C_{A^-}}{C_{\mathrm{H}A}} = K_a \qquad (1)$$

or

$$C_{\mathrm{H}^+} = \frac{C_{\mathrm{H}A}}{C_{A^-}} K_a \qquad (2)$$

If we denote the analytical concentration of the acid by C_a, and that of the salt by C_s, then the concentration of the un-ionized part of the acid (C_{HA}) is $C_a - C_{H^+}$, and that of the anions (A^-) is $C_s + C_{H^+}$. Therefore, in place of equation (2) we may write:

$$C_{H^+} = \frac{C_a - C_{H^+}}{C_s + C_{H^+}} K_a \tag{3}$$

In order to avoid solving the quadratic equation (3), as a rule it can be transformed into a simpler, though approximate, form. In a mixture of a weak acid and its salt the ionization of the acid is greatly repressed by the common-ion effect, and hence for most practical purposes C_{H^+} is negligibly small in comparison to C_a and C_s. Therefore, equation (3) becomes:

$$C_{H^+} = \frac{C_a}{C_s} K_a \tag{4}$$

or

$$pH = \log \frac{1}{C_{H^+}}$$

$$= \log \frac{C_s}{C_a} + pK_a \tag{5}$$

where pK_a is the negative logarithm of the ionization constant.

A study of the titration curve of acetic acid *vs.* sodium hydroxide, Fig. 18, page 205, will afford an explanation of the mechanism by which buffer action is achieved. You will notice that along the middle portion of the first half of this curve, i.e., at 12.5 ml. NaOH where the acid is *half neutralized*, the pH changes very little for each additional ml. of base added. At this point C_a and C_s are equal. Hence, $C_{H^+} = K_a$ or $pH = pK_a$. Here the change of pH for a certain addition of base (or acid) is smaller than at any other point on the curve. Such systems have the ability to take up a considerable quantity of either acid or base without changing appreciably in pH, i.e., they exhibit buffer action and are called buffer solutions.

If the solutions which are encountered in chemical processes, in bacteriological and pathological work, etc., were always solutions of known pure acids and alkalies, the pH value could be calculated from the titration values and ionization constants. This situation is seldom encountered, however, as the solutions normally contain indefinite quantities of other substances, and usually a number of unknown impurities. Many, and in fact most, of these materials have buffer action. This action can best be illustrated by means of an example. Pure water, as stated above, has a *p*H value of 7.0. If 1 cc. of 0.01 *N* HCl is added to a liter of pure water, the *p*H value will be changed to about 5. Let us now consider a solution containing a mixture of sodium acetate and acetic acid. In this solution the dissociation of the acetic acid is very small.

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

The dissociation of sodium acetate is, however, large:

$$CH_3COONa \rightleftharpoons CH_3COO^- + Na^+$$

Now suppose that we add a small quantity of HCl to this solution. It is immediately largely dissociated into H^+ and Cl^- ions:

$$HCl \rightleftharpoons H^+ + Cl^-$$

We therefore have in solution H^+, Cl^-, Na^+, and CH_3COO^- ions. Acetic acid ionizes to only a very slight extent. This means that H^+ and CH_3COO^- ions cannot exist together in solution to a very large extent. Therefore, the larger part of the H^+ ions from the HCl will immediately combine with CH_3COO^- ions to form undissociated molecules of acetic acid, and the H^+ ion concentration or *p*H value of the solution will be only very slightly changed, if at all. If, on the other hand, NaOH is added to this mixture, it dissociates into Na^+ and OH^- ions:

$$NaOH \rightleftharpoons Na^+ + OH^-$$

The OH^- ions then react with the H^+ ions from the acetic acid to form water. More acetic acid will then dissociate into H^+ and CH_3COO^- ions and the H^+ ion concentration will be practically the same as it was before. It will, therefore, be seen that considable quantities of acids or alkalies may be added to solutions containing buffer salts without greatly changing the *p*H value. Since this is true, it is clear that buffered solutions can be diluted with distilled water, even though the water shows a very acid reaction, without materially affecting the *p*H value. In fact, some solutions can be diluted as much as 1000 to 1. This is of importance in making determinations on very highly colored or turbid solutions. In the use of buffer solutions it is essential to remember that they control only the *ratio* between the concentrations of the "acid" and the "basic" color-forms of the indicator. See equations (3) and (4) on page 194.

In general, the salt of any weak acid or weak base is a buffer salt. Very few solutions, therefore, are free from buffer action. For example, the phosphates in raw sugar and culture media, carbonates in raw water, alum and rosin in paper sizing, etc., have buffer action.

In order to bring out the importance of making *p*H determinations rather than determining the total acidity or alkalinity by titration, we shall consider a solution of raw sugar, which contains phosphates as well as other buffer compounds. By the addition of small amounts of acid or alkaline materials, the total acidity or alkalinity is increased, and this additional acid or alkali is shown by titration. Since the solution is highly buffered, however, there will be practically no change in the *p*H value. Since it is the *p*H of the solution, that is, the amount of ionized acid, which determines the amount of inversion of cane sugar, the reason for determining the *p*H rather than the total acidity is apparent. The figures given in Table XII are actual determinations which were made on liquors in a sugar refinery.

TABLE XII *

Per Cent Acidity by Titration	*p*H Values	Per Cent Alkalinity by Titration	*p*H Values
0.001	6.5	0.001	8.3
0.010	6.4	0.003	7.3
0.005	5.3		
0.005	7.0		

* From "The A B C of *p*H Control."

In the first pair of figures, the acidity of the second liquor is 10 times that of the first one, as determined by titration. The *p*H values of the two are, however, practically the same. In the second pair of figures both have an acidity by titration of 0.005 per cent, while the *p*H values show the acidity of the first to be much higher (in fact almost 100 times greater) than the second. The third pair of figures shows even greater discrepancy. By titration the second solution is 3 times as alkaline as the first. By *p*H measurements, however, the first is 10 times more alkaline than the second. While these figures represent measurements on sugar liquors, solutions from other processes show similar variations. The point to be emphasized is that the *p*H value, and not the total acidity or alkalinity obtained by titration, is the important factor in chemical processes, in bacteriological and pathological work, etc.

Unbuffered Solutions.[5] From the above discussion it will be realized that no special precautions are necessary in making *p*H measurements on buffered solutions, since the addition of considerable amounts of acid or alkali can be made without affecting their *p*H value. However, this is not true with distilled water or with unbuffered solutions, especially when their *p*H value is near the neutral point of 7.0. The fact that distilled water is one of the most difficult materials for *p*H determination is frequently overlooked. This is because it is completely devoid of any buffering action, and is thus very susceptible to change during the measurement, for example, by the absorption of carbon dioxide, etc. Pure distilled water is, of course, free from salts and has a *p*H value of 7.0 at 22° C. However, the reaction of ordinary distilled water is always acid, because of the absorption of carbon dioxide. Water which has taken up carbon dioxide from the air until equilibrium has been established will contain about 0.03 per cent of CO_2 by volume, and the calculated *p*H should be 5.7. In fact, this is the value which is usually found in distilled water which has been freely exposed to air. Water from an efficient automatic still, when stored in closed non-soluble glass vessels, will have a *p*H of 6.0 to 6.4. If this water is boiled for a short time in a pyrex vessel, and the vessel then fitted with a soda-lime tube, it will usually have a *p*H of 6.6 to 6.8.

When it is necessary to make a solution of an unbuffered material in order to determine its *p*H value, the water used should be as nearly neutral as possible, since any acidity of the water will affect the *p*H of the dissolved material. Water having a *p*H value of 6.6 to 6.8 is satisfactory for this work. In making these solutions, the proportion of material to water should always be kept the same, so that different determinations will be comparable.

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[5] "The A B C of *p*H Control"; see also, Yoe, "Photometric Chemical Analysis," Vol. I, p. 204, John Wiley & Sons, New York, 1928.

It is equally true that the indicator solutions should have a neutral reaction, since any excess acid or alkali will likewise change the *p*H value of the material. These precautions are particularly important when the *p*H value of the material is near 7.0. Near this point small variations in hydrogen-ion concentration, due to absorption of carbon dioxide, etc., have a marked effect on the *p*H value. This effect is much less marked when the material has a *p*H below 6 or above 8.

In making a *p*H measurement on distilled water or unbuffered solutions, the indicator and the material being tested should always be mixed in the test tube by means of a stirring rod, with the minimum of exposure to air, and readings should be made at once. If this is done, reliable results will be secured with the colorimetric method. Potentiometric methods as ordinarily made are very unreliable when applied to most unbuffered solutions.

PROBLEMS

1. A 0.1 *M* HCl solution is 92 per cent ionized. What are its H^+ ion and OH^- ion concentrations, respectively?

Ans. 9.2×10^{-2}, 1.1×10^{-13}.

2. A 0.1 *M* NH_4OH solution is 4.1 per cent ionized. What are its H^+ ion and OH^- ion concentrations, respectively?

Ans. 2.4×10^{-12}, 4.1×10^{-3}.

3. Express the following H^+ ion concentrations in terms of *p*H: (*a*) 1×10^{-3}, (*b*) 1×10^{-5}, (*c*) 1×10^{-8}, (*d*) 1×10^{-10}, and (*e*) 1×10^{-14}.

Ans. (*a*) 3. (*d*) 10.
(*b*) 5. (*e*) 14.
(*c*) 8.

4. Calculate the *p*H of each of the following solutions, their H^+ ion concentration being given: (*a*) 2.5×10^{-4}, (*b*) 6.8×10^{-7}, (*c*) 9.3×10^{-10}, (*d*) 4.7×10^{-12} and (*e*) 1.9×10^{-13}.

Ans. (*a*) 3.6. (*d*) 11.3.
(*b*) 6.2. (*e*) 12.7.
(*c*) 9.0.

5. What is the *p*OH value of each solution in problem 4?

Ans. (*a*) 10.4. (*d*) 2.7.
(*b*) 7.8. (*e*) 1.3.
(*c*) 5.0.

6. Calculate the H^+ ion concentrations of solutions whose *p*H values are the following: (*a*) 1.5, (*b*) 4.8, (*c*) 7.9, (*d*) 10.2, and (*e*) 13.6.

Ans. (*a*) 3.2×10^{-2}. (*d*) 6.3×10^{-11}.
(*b*) 1.6×10^{-5}. (*e*) 2.5×10^{-14}.
(*c*) 1.3×10^{-8}.

7. Calculate the pH of 0.01 M $HC_2H_3O_2$ solution which is 4.17 per cent ionized at 18° C.

Ans. 3.38.

8. A solution of 0.01 M $HCHO_2$ is 13.4 per cent ionized at 25° C. What What are the pH and pOH of the solution?

Ans. 2.87, 11.13.

9. What is the pH of a 1.0 M solution of HCl which is 80 per cent ionized?

Ans. 0.10.

10. Calculate the pH of 1.0 M NH_4OH solution which is 0.42 per cent ionized. What is its pOH?

Ans. 11.62, 2.38.

11. A liter of water saturated with H_2S at 25° C. under 1 atmosphere of pressure contains 1.2×10^{-15} gram-ion of $S^{=}$ ion. What is the H^+ ion concentration of the solution? What is its pH? $K_{(H_2S)} = 1.1 \times 10^{-23}$.

Ans. (*a*) 9.6×10^{-5}.
(*b*) 4.02.

12. What pH would be required to lower the sulfide concentration to 1×10^{-20} in the solution given in problem 11?

Ans. 1.48.

13. If 0.1 mol of NH_4Cl is added to a liter of 0.01 M NH_4OH, what would be the pH of the solution? The NH_4Cl is 85 per cent ionized; 0.01 M NH_4OH is 4.1 per cent ionized at 18° C.; $K_{(\text{ion})}$ of NH_4OH is 1.75×10^{-5}.

Ans. 8.31.

14. What is the pH of a solution made by mixing 500 ml. of 0.2 M $HC_2H_3O_2$ and 500 ml. of 0.2 M $NaC_2H_3O_2$? Consult tables for the data required to solve this problem. Assume that the solution temperature is 18° C.

Ans. 4.62.

15. To a liter of 0.01 M solution of $HCHO_2$ are added 6.8 grams of $NaCHO_2$. What was the pH of the formic acid solution (*a*) before and (*b*) after adding the salt? One-tenth M $NaCHO_2$ is 85 per cent ionized.

Ans. (*a*) 2.87.
(*b*) 4.63.

NEUTRALIZATION

We have already discussed the ionization of acids and bases. We learned that the strength of an acid or a base depends upon its degree of ionization in aqueous solution. A strong acid or base is defined as one which is highly dissociated in water solution, and, conversely, a weak acid or base is one which is slightly dissociated in aqueous solution. Neutralization is the reaction between acids and bases which results in the formation of water and a salt of the respective acid and base. Since some acids are strong and some are weak, and likewise bases may be either strong or weak, it follows that there are four general types of neutralization reactions:

1. Neutralization of a strong acid with a strong base.

   Example: $HCl + NaOH \rightarrow NaCl + H_2O$.

2. Neutralization of a strong acid with a weak base.

   Example: $HCl + NH_4OH \rightarrow NH_4Cl + H_2O$.

3. Neutralization of a weak acid with a strong base.

   Example: $HCN + NaOH \rightarrow NaCN + H_2O$.

4. Neutralization of a weak acid with a weak base.

   Example: $HCN + NH_4OH \rightarrow NH_4CN + H_2O$.

As the above four equations are written it appears that all run to completion. This is not true, and the reason is that they are all carried out in water solutions and hence it is impossible for any neutralization reaction to go to 100 per cent completion. Water is always slightly ionized, and hence its equilibrium constant must be satisfied in all neutralization reactions. Its ionic reaction is

$$HOH \rightleftharpoons H^+ + OH^-$$

and at equilibrium the following relationship holds:

$$C_{H^+} \times C_{OH^-} = K_w = 1.0 \times 10^{-14} \quad (25° \text{ C.})$$

$$C_{H^+} = C_{OH^-} = 10^{-7}$$

Hence, in all neutralization reactions there are always present **both** H^+ ions and OH^- ions. Whether the solution obtained by mixing equivalent quantities of an acid and a base will be acid, alkaline, or neutral depends entirely upon the relative strengths of the acid and base, i.e., their degrees of ionization.

1. A strong acid neutralized with a strong base.

If the acid and base are completely ionized at the start of the reaction or if they are ionized to exactly the same extent (say 90 per cent), then the resulting salt solution will have a *p*H value of 7.0, and the solution will be neutral. In other words, the reaction proceeds until the concentration of H^+ ion and of OH^-

ion is 10^{-7} gram-ion per liter, the H^+ ion and OH^- ion concentration in pure water.

$$\begin{array}{lll} HCl \rightleftharpoons & H^+ & + Cl^- \\ NaOH \rightleftharpoons & OH^- & + Na^+ \\ & \upharpoonleft\downharpoonright & \\ & HOH & \end{array}$$

Solution is neutral.

Only one equilibrium constant must be satisfied, namely,

$$C_{H^+} \times C_{OH^-} = K_w = 1.0 \times 10^{-14}$$

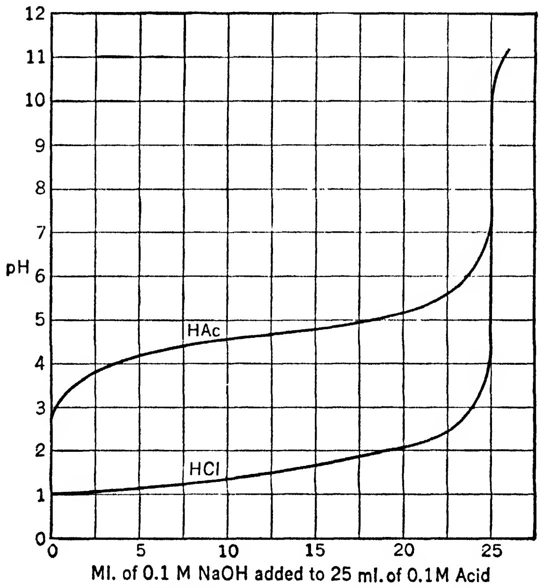
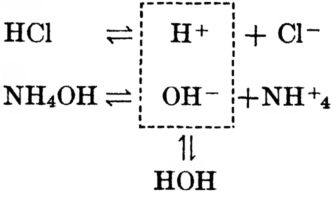


Fig. 18.—Titration Curves

Figure 18 shows graphically the change in *p*H during the titration of 25 ml. of 0.1 *M* HCl with 0.1 *M* NaOH. Note that the *p*H changes very little until almost exactly at the *equivalence-point*, where the change is enormous.

2. A strong acid neutralized with a weak base.

In all such neutralization reactions two ionization constants must be satisfied, namely, $C_{H^+} \times C_{OH^-} = K_w$ and the $K_{(ion)}$ of the base. For example,



Solution is acid.

The joint equilibria which must be satisfied are:

$$\frac{C_{NH_4^+} \times C_{OH^-}}{C_{NH_4OH}} = 1.75 \times 10^{-5} \qquad (1)$$

and

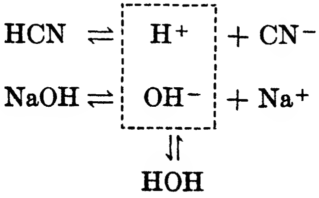
$$C_{H^+} \times C_{OH^-} = 1.0 \times 10^{-14} \qquad (2)$$

When equilibrium is reached, some non-ionized NH_4OH must be present to satisfy the ammonium hydroxide equilibrium (equation [1]), and this lowers the concentration of OH^- ions, leaving an excess of H^+ ions. Therefore, at equilibrium the solution will be acid, and its *p*H value will be less than 7.

In general, if the base has a lower degree of ionization than the acid, the salt solution obtained upon neutralization will be acid, having at equilibrium a *p*H less than 7. Make a graph showing the change in *p*H upon titrating a strong acid with a weak base.

3. A weak acid neutralized with a strong base.

This process is just the reverse of the preceding one, but it also must satisfy two ionization constants, namely, $C_{H^+} \times C_{OH} = K_w$ and the $K_{(ion)}$ of the acid. For example,



Solution is alkaline.

The two equilibria which must be satisfied are:

$$\frac{C_{H^+} \times C_{CN^-}}{C_{HCN}} = 7.2 \times 10^{-10} \qquad (1)$$

and

$$C_{H^+} \times C_{OH^-} = 1.0 \times 10^{-14} \qquad (2)$$

When equilibrium is reached, some of the non-ionized HCN must be present to satisfy the hydrocyanic acid equilibrium (equation [1]), and this lowers the H^+ ion concentration, leaving an excess of OH^- ions. Therefore, at equilibrium the solution will be alkaline, and its *p*H value will be greater than 7.

In all neutralizations, when the acid has a smaller degree of ionization than the base, the salt solution obtained at equilibrium will be alkaline, having a *p*H greater than 7. Figure 18 shows graphically the change in *p*H during the titration of 25 ml. of 0.1 *M* HAc with 0.1 *M* NaOH. Note that at the point where the acid is *half neutralized,* the *p*H changes very little for each additional milliliter of NaOH added, i.e., this is the point of maximum buffer action.

4. Neutralization of a weak acid with a weak base.

In the neutralization of a weak acid with a weak base, and *vice versa,* three ionization constants must be satisfied, namely, K_w, $K_{(\text{ion})}$ of the acid, and $K_{(\text{ion})}$ of the base. For example,

$$\begin{array}{llcl} \mathrm{HCN} & \rightleftharpoons & \mathrm{H^+} & + \mathrm{CN^-} \\ \mathrm{NH_4OH} & \rightleftharpoons & \mathrm{OH^-} & + \mathrm{NH_4^+} \\ & & \downarrow\uparrow & \\ & & \mathrm{HOH} & \end{array}$$

Solution is alkaline, because the degree of ionization of the base is greater than that of the acid.

At equilibrium, the following equations must be satisfied simultaneously:

$$\frac{C_{\mathrm{H^+}} \times C_{\mathrm{CN^-}}}{C_{\mathrm{HCN}}} = K_a = 7.2 \times 10^{-10} \tag{1}$$

$$\frac{C_{\mathrm{NH_4^+}} \times C_{\mathrm{OH^-}}}{C_{\mathrm{NH_4OH}}} = K_b = 1.75 \times 10^{-5} \tag{2}$$

and

$$C_{\mathrm{H^+}} \times C_{\mathrm{OH^-}} = K_w = 1.0 \times 10^{-14} \tag{3}$$

In all neutralizations involving reactions between a weak acid and a weak base, the salt solution resulting at equilibrium will be acid, alkaline, or neutral depending upon the relative magnitudes of the ionization constants of the acid and base, which in turn depend upon the respective degrees of ionization. In the reaction between HCN and NH_4OH, the base is more ionized that the acid and hence the salt solution at equilibrium is alkaline. But with $HC_2H_3O_2$ and NH_4OH the values for K_a and K_b are almost identical, and, hence, at the equilibrium point their salt solution will be approximately neutral, and have a pH close to 7. In general, when the acid is weaker than the base, the equilibrium solution will be alkaline, its $p\text{H} > 7$; and when the reverse is true, the equilibrium solution will be acid, its $p\text{H} < 7$. When the acid is exactly as weak as the base, the equilibrium solution will be neutral, and its $p\text{H} = 7$.

HYDROLYSIS

The phenomenon of hydrolysis may be considered the reverse of neutralization. Instead of an acid and base reacting to form a salt and water as in neutralization reactions, in the process of hydrolysis a salt and water interact to form an acid and a base. The interrelationship between neutralization and hydrolysis may be illustrated by considering the following two reactions in which HA represents any acid and BOH is any base:

$$\text{(Neutralization)}\quad \text{H}A + B\text{OH} = BA + \text{HOH} \qquad (1)$$

$$\text{(Hydrolysis)}\quad BA + \text{HOH} = \text{H}A + B\text{OH} \qquad (2)$$

At equilibrium, the rate at which HA and BOH interact to form BA and HOH is equal to the rate at which BA and HOH interact to form HA and BOH. Hence, the equilibrium condition may be represented by combining reactions (1) and (2), using arrows pointing in opposite directions as follows:

$$\underset{\xrightarrow[\text{Neutralization}]{}}{\text{H}A + B\text{OH}} \rightleftharpoons \underset{\xleftarrow[\text{Hydrolysis}]{}}{BA + \text{HOH}} \qquad (3)$$

The extent to which a salt will hydrolyze depends upon the relative degrees of ionization of the acid and base formed, which in turn depend upon the relative strengths of the acid and base. If the acid formed is weaker than the base, then it will tie up some of the H^+ ions of the water in forming non-ionized acid molecules, leaving an excess of OH^- ions in the solution when the equilibrium conditions have been satisfied. Such solutions, therefore, will be alkaline. If, on the other hand, the base is weaker than the acid, then the base will tie up some of the OH^- ions of the water in order to produce non-ionized base molecules, leaving an excess of

H^+ ions in the solution when equilibrium is attained. Hence, such solutions will be acid. Finally, when the acid and base are of equal strength, the hydrolysis of their salt results in the formation of a neutral solution. However, it must be emphasized that the degree of hydrolysis is not indicated by acidity or alkalinity of the resulting solution alone. For example, NaCl undergoes practically no hydrolysis and its aqueous solution is neutral. On the other hand, $NH_4C_2H_3O_2$ undergoes appreciable hydrolysis and yet its aqueous solution is very nearly neutral. The degree or extent to which a salt hydrolyzes is expressed by the ratio: $\frac{\text{Amount of salt hydrolyzed}}{\text{Original amount of salt}}$. Multiplying this ratio by 100 gives the percentage hydrolyzed. At room temperature NH_4CN is almost 100 per cent hydrolyzed.

Let us now consider the four types of hydrolysis and show how the degree of hydrolysis can be determined. For the sake of simplicity, we will use the four salts formed in the neutralization reactions given on page 204, namely, NaCl, NH_4Cl, NaCN, and NH_4CN.

1. Hydrolysis of a salt of a strong acid and a strong base. Example: NaCl.

$$NaCl \rightleftharpoons Na^+ + Cl^-$$

$$HOH \rightleftharpoons OH^- + H^+$$

The NaCl yields Na^+ ions and Cl^- ions on dissociation. In the presence of H^+ ions and OH^- ions from the water, it is possible for HCl and NaOH to form. However, both acid and base are highly ionized and to the same degree. Consequently the original H^+ ion and OH^- ion concentration of the water remains unchanged and hence the solution will be neutral. Likewise, the Na^+ ions and Cl^- ions remain practically unchanged, and hence hydrolysis is negligibly small.

2. Hydrolysis of a salt of a strong acid and a weak base. Example: NH_4Cl.

$$\begin{tikzcd}[row sep=small]
NH_4Cl \rightleftharpoons & NH_4^+ & + Cl^- \\
HOH \rightleftharpoons & OH^- \arrow[d, shift left] & + H^+ \\
& NH_4OH \arrow[u, shift left] &
\end{tikzcd}$$

The H^+ ions and Cl^- ions do not unite because HCl is a strong acid. But NH_4OH is a weak base and hence some of the NH_4^+ ions will unit with OH^- ions to form non-ionized NH_4OH. This results in a removal of OH^- ions and causes more water to ionize. The process continues until the ionization constants both for NH_4OH and for water are satisfied. H^+ ions are then in excess and the solution has an acid reaction—its pH < 7. The hydrolysis equilibrium is expressed by the following ratio:

$$\frac{C_{H^+} \times C_{OH^-}}{\dfrac{C_{NH_4^+} \times C_{OH^-}}{C_{NH_4OH}}} = \frac{K_w}{K_{\text{base}}} = K_{(\text{hyd.})} \tag{1}$$

By division the equation simplifies to

$$\frac{C_{H^+} \times C_{NH_4OH}}{C_{NH_4^+}} = \frac{K_w}{K_{\text{base}}} = K_{(\text{hyd.})} \tag{2}$$

Case 33. Hydrolysis Calculations.

Example 1. Calculate the hydrolysis constant of a 0.1 M solution of NH_4Cl.

The hydrolysis constant is the ratio of K_w to the $K_{(\text{ion})}$ for NH_4OH. Hence,

$$\frac{K_w}{K_{\text{base}}} = \frac{1.0 \times 10^{-14}}{1.75 \times 10^{-5}} = 5.7 \times 10^{-10}$$

$$\therefore \quad K_{(\text{hyd.})} \text{ of } NH_4Cl = 5.7 \times 10^{-10}$$

Example 2. Calculate the H^+ ion concentration in a 0.1 M solution of NH_4Cl after hydrolysis has reached equilibrium. Assume complete ionization of the NH_4Cl. $K_{(\text{hyd.})}$ of $NH_4Cl = 5.7 \times 10^{-10}$.

The equilibrium condition expressed in equation (2) must be satisfied.

$$\frac{C_{H^+} \times C_{NH_4OH}}{C_{NH_4^+}} = 5.7 \times 10^{-10}$$

Let $x = C_{H^+}$ at equilibrium and also the C_{NH_4OH} formed by hydrolysis. $(0.1 - x)$ will equal the NH_4^+ ion concentration at equilibrium. Substituting these values in the above expression, we get

$$\frac{x \times x}{(0.1 - x)} = 5.7 \times 10^{-10}$$

$(0.1 - x)$ will be only slightly different from 0.1, the original concentration of NH_4Cl. Hence,

$$\frac{x^2}{0.1} = 5.7 \times 10^{-10}$$

$$x^2 = 5.7 \times 10^{-11}$$

$$x = 7.5 \times 10^{-6}$$

Therefore, the H^+ ion concentration is 7.5×10^{-6} gram-ion per liter. The concentration of non-ionized NH_4OH formed by hydrolysis is also equal to x, or 7.5×10^{-6} gram-mol per liter.

Example 3. Calculate the degree of hydrolysis of 0.1 M NH_4Cl.

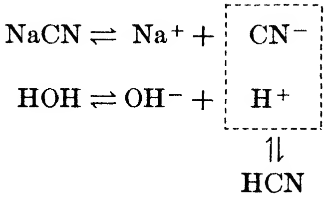
If this solution were 100 per cent hydrolyzed, there would be 0.1 gram-mol of NH_4OH per liter. However, in example 2 the total concentration of NH_4OH was calculated to be 7.5×10^{-6} gram-mol per liter. Therefore the degree of hydrolysis is

$$\frac{7.5 \times 10^{-6}}{0.1} = 7.5 \times 10^{-5}$$

or

$$7.5 \times 10^{-5} \times 100 = 7.5 \times 10^{-3} \text{ per cent hydrolysis}$$

3. Hydrolysis of a salt of a weak acid and a strong base. Example: NaCN.



$$\begin{array}{l} NaCN \rightleftharpoons Na^+ + \boxed{\begin{array}{c} CN^- \\ \\ H^+ \end{array}} \\ HOH \rightleftharpoons OH^- + \\ \qquad\qquad\qquad\quad \upharpoonleft\downharpoonright \\ \qquad\qquad\qquad\quad HCN \end{array}$$

The Na^+ ions and OH^- ions do not combine because NaOH is a strong base. But HCN is a weak acid and hence some of the H^+ ions will unite with CN^- ions to form non-ionized HCN. This removes H^+ ions from solution and consequently more water dissociates. The process continues until the K_w value for water is re-established and the $K_{(\text{ion})}$ of HCN is reached. At the equilibrium point OH^- ions will be in excess and hence the solution will have an alkaline reaction, its $pH > 7$. The hydrolysis equilibrium is expressed by the following ratio:

$$\frac{C_{H^+} \times C_{OH^-}}{\dfrac{C_{H^+} \times C_{CN^-}}{C_{HCN}}} = \frac{K_w}{K_{\text{acid}}} = K_{(\text{hyd.})} \tag{3}$$

By division the equation simplifies to

$$\frac{C_{OH^-} \times C_{HCN}}{C_{CN^-}} = \frac{K_w}{K_{\text{acid}}} = K_{(\text{hyd.})} \tag{4}$$

4. Hydrolysis of a salt of a weak acid and a weak base. Example: NH_4CN.

$$\begin{array}{rcccc} NH_4CN \rightleftharpoons & NH_4^+ & + & CN^- \\ HOH \rightleftharpoons & OH^- & + & H^+ \\ & \downarrow\uparrow & & \downarrow\uparrow \\ & NH_4OH & & HCN \end{array}$$

In the hydrolysis of salts of this type, three constants must be satisfied before the solution reaches equilibrium. These are K_w, $K_{(\text{ion})}$ of the acid, and $K_{(\text{ion})}$ of the base. The equilibrium expression for the hydrolysis of NH_4CN is as follows:

$$\frac{C_{H^+} \times C_{OH^-}}{\dfrac{C_{H^+} \times C_{CN^-}}{C_{HCN}} \times \dfrac{C_{NH_4^+} \times C_{OH^-}}{C_{NH_4OH}}} = \frac{K_w}{K_{\text{acid}} \times K_{\text{base}}} = K_{(\text{hyd.})} \qquad (5)$$

Upon dividing we get

$$\frac{C_{HCN} \times C_{NH_4OH}}{C_{CN^-} \times C_{NH_4^+}} = \frac{K_w}{K_{\text{acid}} \times K_{\text{base}}} = K_{(\text{hyd.})} \qquad (6)$$

By applying equation (6) to salts of the above type, we can obtain the concentration of the anions or cations present when hydrolysis has reached equilibrium.

PROBLEMS

1. When equivalent quantities of potassium hydroxide and nitric acid solutions are mixed, will the resulting solution be acid, alkaline, or neutral? Write the ionic equation for the reaction.

2. Lithium hydroxide and formic acid solutions are mixed in equivalent amounts. Is the resulting solution acid, alkaline, or neutral? Write the ionic equation for the reaction.

3. If 50.0 ml. of 0.5 *M* H_2SO_4 are mixed with 50.0 ml. of 0.5 *M* NH_4OH, will the resulting solution have a *p*H equal to 7, greater than 7, or less than 7? Write the ionic equation for the reaction.

4. Equivalent weights of hydrazine, $NH_2 \cdot NH_2$, and hydrochloric acid are mixed in aqueous solution. Will the solution thus formed have an acid, an alkaline, or a neutral reaction? Write the ionic equation for the reaction.

5. How many milliliters of 0.5 *M* KOH solution are required to neutralize 25 0 ml. of each of the following acid solutions: (*a*) 0.5 *M* $HClO_4$, (*b*) 0.5 *M* H_2SO_4, (*c*) 0.5 *M* H_3PO_4?

6. How many milliliters of 0.1 *M* NaOH solution are required to neutralize 10.0 ml. of each of the following acids: (*a*) 0.3 *M* HCl, (*b*) 0.15 *M* H_2SO_4, and (*c*) 0.1 *M* H_3PO_4?

7. How many milliliters of 0.05 *M* H_2SO_4 solution are required to neutralize 25.0 ml. of each of the following alkali solutions: (*a*) 0.1 *M* NH_4OH, (*b*) 0.1 *M* NaOH, and (*c*) 0.05 *M* $Ca(OH)_2$?

8. How many milliliters of 1.0 *M* $HClO_4$ solution are equivalent to 0.1 mol of the following bases: (*a*) LiOH, (*b*) $Be(OH)_2$, (*c*) $Al(OH)_3$, and (*d*) $Ce(OH)_4$?

9. Calculate the hydrolysis constant of a 0.1 *M* solution of $KC_2H_3O_2$. $K_w = 1.0 \times 10^{-14}$ and $K_{(\text{ion})}$ for $HC_2H_3O_2 = 1.86 \times 10^{-5}$.

Ans. 5.4×10^{-10}.

10. What is the value of $K_{(\text{hyd.})}$ of 0.1 *M* NH_4Cl? $K_w = 1.0 \times 10^{-14}$ and $K_{(\text{ion})}$ for $NH_4OH = 1.75 \times 10^{-5}$.

Ans. 5.7×10^{-10}.✓

11. (*a*) Derive the equilibrium expression for the hydrolysis constant of KCN. (*b*) Write the general formula for the hydrolysis of salts of this type.

12. (*a*) Derive the equilibrium equation for $K_{(\text{hyd.})}$ of NH_4NO_3. (*b*) Write the general expression for the hydrolysis of salts of this type.

13. Derive the general equation for the hydrolysis constant of a salt formed by the neutralization of a weak base by a weak acid.

14. Write ionic equations representing the hydrolysis of the following salts, and state whether the solutions are acid, alkaline, or neutral: (*a*) KCl, (*b*) $NaCHO_2$, (*c*) $CuSO_4$, (*d*) $FeCl_3$, (*e*) KCN.

15. Calculate the H^+ ion concentration of a 0.01 *M* solution of NH_4Cl. $K_w = 1.0 \times 10^{-14}$ and $K_{(\text{hyd.})}$ of $NH_4Cl = 5.7 \times 10^{-10}$.

Ans. 2.4×10^{-6}.

16. What will be the concentration of non-ionized NH_4OH formed by the hydrolysis of a 0.01 *M* solution of NH_4Cl?

Ans. 2.4×10^{-6}.

17. (*a*) Calculate the degree of hydrolysis of 0.01 *M* NH_4Cl. (*b*) What is the percentage hydrolysis?

Ans. (*a*) 2.4×10^{-4}. (*b*) 2.4×10^{-2}.

18. What are the concentrations of $NH_4{}^+$ ion and of CN^- ion in a 0.1 *M* solution of NH_4CN after hydrolysis has reached equilibrium? $K_w = 1.0 \times 10^{-14}$, $K_a = 7.2 \times 10^{-10}$, and $K_b = 1.75 \times 10^{-5}$.

Ans. (*a*) 5.3×10^{-2}. (*b*) 5.3×10^{-2}.

19. (*a*) Calculate the degree of hydrolysis of NH_4CN in 0.1 *M* solution. (*b*) What is its percentage of hydrolysis?

Ans. (*a*) 0.47. (*b*) 47.

20. Calculate the hydrolysis constant for each of the following salts: (*a*) KCN, (*b*) $KCHO_2$, and (*c*) NH_4CHO_2.

Ans. (*a*) 1.4×10^{-5}. (*b*) 5×10^{-11}. (*c*) 2.9×10^{-6}.

21. (*a*) What is the OH^- ion concentration in a 0.1 *M* solution of $KC_2H_3O_2$? (*b*) How much non-ionized $HC_2H_3O_2$ is formed by the hydrolysis of the salt?

Ans. (*a*) 7.3×10^{-6} (*b*) 7.3×10^{-6}.

22. A liter of 0.1 *M* $HC_2H_3O_2$ contains 5 mg. of Fe^{+++} ions. How much $NH_4C_2H_3O_2$ must be added to the solution in order to just start the precipitation of $Fe(OH)_3$? Assume that the $NH_4C_2H_3O_2$ is 100 per cent ionized. $K_w = 1.0 \times 10^{-14}$ and $K_{\text{s.p.}}$ of $Fe(OH)_3 = 1.1 \times 10^{-36}$.

Ans. 0.22 g.

23. Will Al_2S_3 and Cr_2S_3 hydrolyze in water? Explain fully.

24. (*a*) The trivalent ions Fe^{+++}, Al^{+++}, and Cr^{+++} may be precipitated as hydroxides by extremely dilute ammonium hydroxide. Explain. (*b*) What is the action of ammonium sulfide upon the mixture thus produced? Explain.

25. Sodium sulfide reagent is 3 *N* in Na_2S, 1 *N* in Na_2S_2, and 1 *N* in NaOH. What is the function of the NaOH in the solution?

CHAPTER XIX

OXIDATION-REDUCTION EQUILIBRIA

We have already defined oxidation as a chemical change in which an atom or ion loses one or more electrons (see page 29). For example,

$$Zn^\circ - 2e \rightarrow Zn^{++}$$

$$Fe^{++} - \ e \rightarrow Fe^{+++}$$

Reduction is just the reverse of oxidation; i.e., an atom or ion gains one or more electrons. For example,

$$Zn^{++} + 2e \rightarrow Zn^\circ$$

$$Fe^{+++} + \ e \rightarrow Fe^{++}$$

These two processes always take place simultaneously and to the same extent. That is to say, for every electron lost by an atom or ion, an electron is gained by some other atom or ion.

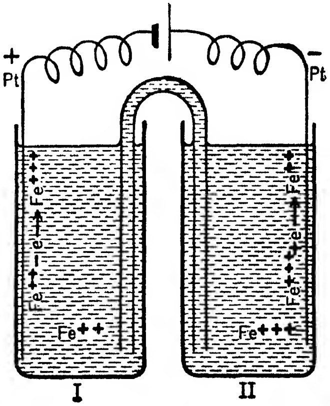


Fig. 19

Since an electric current is a flow of electrons, it should cause an oxidation-reduction reaction to take place. Experiment shows this to be so. For example, suppose we place in vessel I (Fig. 19) a solution of ferrous chloride and in vessel II a solution of ferric chloride. Connect the solutions in vessels I and II by means of an inverted U-tube filled with a solution of potassium chloride. Such a connection is called a "salt bridge." Now introduce into vessel I a platinum wire connected to the + pole of a battery and into vessel II a platinum wire connected to the − pole. As the current passes through the two solutions, ferrous ions are oxidized at the anode ($Fe^{++} - e \rightarrow Fe^{+++}$) and ferric ions are reduced at the cathode ($Fe^{+++} + e \rightarrow Fe^{++}$). This may be readily shown by removing a small portion of the solution from each vessel and testing I for ferric ions and II for ferrous ions. Since only the electric current, i.e., a stream of electrons, has passed through the solutions, it is obvious that the oxidation in vessel I was due to a loss of electrons and that the reduction in II was due to a gain in electrons. Hence, we may say that, in electrolysis, oxidation is the chemical change which takes place at the anode and reduction the chemical change simultaneously taking place at the cathode.

In this experiment the oxidation-reduction was produced by the electric current. Conversely, it should be possible to produce an electric current by means of an oxidation-reduction reaction. This is indeed true, provided the reactions are carried out in such a manner that the energy which they evolve takes the form of electricity instead of heat. In order to accomplish this, the solutions must be prevented from mixing and the transfer of electrons from the reductant to the oxidant must be accomplished by means of a suitable conductor placed outside the solutions. All electric batteries are arranged in this way, one of the oldest and simplest being the Daniell cell.

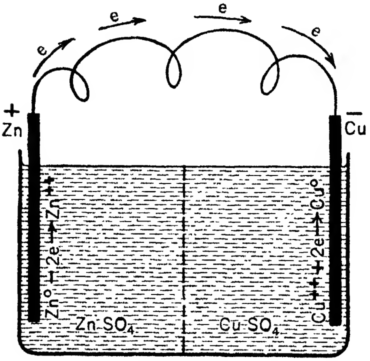


FIG. 20

The Daniell Cell. This cell (Fig. 20) consists of a zinc electrode immersed in a zinc sulfate solution and a copper electrode immersed in a copper sulfate solution. The two solutions are separated by a porous partition represented by the broken line in the figure. By this arrangement, the two solutions are kept in electrical contact without appreciable mixing. The zinc atoms of the zinc electrode have a tendency to lose their two valence electrons and to pass into the solution as zinc ions. This leaves the zinc electrode negatively charged. At the copper electrode there is a tendency for the copper ions to take two electrons from the electrode and thus form copper atoms. Consequently the copper electrode becomes positively charged. These reactions soon build up electric charges on the electrodes which prevent further action. If now the two electrodes be connected with a wire, the electrons will pass from the zinc electrode to the copper electrode, and as the charges on the electrodes are removed, the reactions proceed; i.e., an electric current flows.

Equilibrium between a Metal and Its Ions. The reactions which take at the two electrodes of the Daniell cell are characteristic of all electrodes, and the potential developed at each electrode is called a "single electrode potential." In 1889 Nernst suggested a theory to explain the nature of the single electrode potential, namely, that the atoms of an electrode have a definite tendency to pass into solution as ions, and the ions in solution have a definite tendency to deposit on the electrode as atoms. The tendency or force which causes the electrode atoms to give up electrons and to pass into solution as ions is looked upon as a kind of pressure and is called the **electrolytic solution pressure** (P). This pressure is determined by the effective concentration of the ions, which in dilute solution is proportional to the **osmotic pressure** (p) of the solution. Three conditions are possible, namely, $P > p$, $P = p$, and $P < p$. These conditions are represented diagrammatically in Fig. 21.[1] If $P > p$, a certain amount of the metal will go into

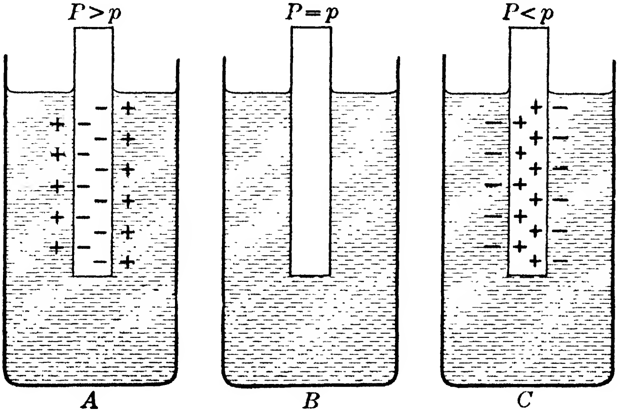


FIG. 21

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[1] Similar to Fig. 133 in Getman and Daniels, "Outlines of Theoretical Chemistry," fifth edition, John Wiley & Sons, New York, 1931.

solution in the ionic state; if $P < p$, metal atoms will deposit out of solution; and if $P = p$, the metallic ions will form at the same rate at which metal atoms are deposited. When $P > p$, the solution acquires a positive charge and the metal a negative one. When $P < p$, the solution becomes negatively and the metal positively charged. If $P = p$, no action takes place and the potential difference between metal and solution is zero.

Let us take an example. Suppose that in vessel *A* in Fig. 21 is a strip of zinc dipping in water. $P > p$. A few of the zinc atoms give up two electrons each and pass into solution as zinc ions, thus leaving the electrode negatively charged and simultaneously causing the layer of solution surrounding the electrode to become positively charged. These two layers of opposite electric charges are called a Helmholtz **electrical double layer,** and their actual existence has been demonstrated by Palmaer.[2] The formation of zinc ions is represented thus:

$$Zn^{\circ} - 2e \rightarrow Zn^{++}$$

The negatively charged strip of zinc will attract the positively charged zinc ions, and consequently a difference of potential will be set up. This electromotive force is called the **electrode potential** of the metal. Only a minute quantity of zinc dissolves in the water, too small to be detected by ordinary chemical tests, and hence the electrolytic solution pressure *P* must be balanced by opposing forces as soon as a relatively small number of zinc ions are formed. The two forces opposing the solution pressure *P* are: (1) the osmotic pressure *p* of the zinc ions in solution and (2) the electrostatic attraction between the positively charged zinc ions and the negative charge on the strip of metallic zinc. The osmotic pressure causes the zinc ions to discharge on the zinc strip according to the equation

$$Zn^{++} + 2e \rightarrow Zn^{\circ}$$

The solution pressure of the zinc is soon balanced by the combined action of the osmotic pressure and the electrostatic force; i.e., equilibrium is quickly attained.

If some zinc salt be dissolved in water and then a strip of zinc dipped into the solution, the zinc ions already present will oppose the solution pressure and consequently fewer zinc ions will pass

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[2] *Z. physik. Chem.*, **25**, 265–283 (1898); **36**, 664–680 (1901).

into solution to establish a balance. Hence, a much smaller electrostatic force, i.e., potential difference, will be required to establish equilibrium. When the concentration of zinc ions is such as to produce an osmotic pressure equal to the electrolytic solution pressure, i.e., $p = P$, then the potential difference will be zero. The equilibrium between the metallic zinc and its ions represents a true chemical equilibrium, that is, the rate of solution is equal to the rate of deposition.

When a metal dissolves to form positively charged ions, the process is one of oxidation, since the positive valence increases from zero to one or more positive charges. Conversely, when a metal is deposited out of a solution of its ions, reduction occurs; i.e., the positive valence is decreased to zero. In such reversible reactions the metal functions as a reducing agent (reductant) and the metallic ions as oxidizing agent (oxidant). Reversible reactions of this type are called half-cell reactions, since two such systems are required to make up a galvanic cell, as for example, the Daniell cell.

Since the dissolving and deposition of zinc constitute a reversible reaction, $\mathrm{Zn}^\circ - 2e \rightleftharpoons \mathrm{Zn}^{++}$, it should reach equilibrium when the concentration of zinc ions reaches a certain definite value, namely, the value which satisfies the equilibrium constant for this reaction. Applying the law of chemical equilibrium to this reaction, we have

$$\frac{C_{\mathrm{Zn}^{++}}}{C_{\mathrm{Zn}^\circ}} = K$$

where K is the equilibrium constant. But since the concentration of atoms in a dense strip of metal is a constant, the equation reduces to

$$C_{\mathrm{Zn}^{++}} = K \times C_{\mathrm{Zn}^\circ} = k_{\mathrm{Zn}^{++}}$$

Likewise, a state of equilibrium between a strip of copper and its ions may be expressed by a reversible equation as follows:

$$\mathrm{Cu}^\circ - 2e \rightleftharpoons \mathrm{Cu}^{++}$$

Applying the law of chemical equilibrium, we get

$$\frac{C_{\mathrm{Cu}^{++}}}{C_{\mathrm{Cu}^\circ}} = K$$

$$C_{\mathrm{Cu}^{++}} = K \times C_{\mathrm{Cu}^\circ} = k_{\mathrm{Cu}^{++}}$$

The above illustrations with zinc and copper are typical. When a metal is placed in a solution of its ions, a potential develops which depends upon two factors: (1) the equilibrium ion concentration of the metal (a constant for each), and (2) the concentration of its ions in the solution. A metal will acquire a positive, a negative, or no electric charge when dipped into a solution of its ions, depending upon whether the ion concentration is greater than, less than, or equal to its equilibrium ion concentration. The greater the difference between the ion concentration in a solution and the equilibrium value for the metal, the greater is the potential difference and, consequently, the greater is the tendency for the reaction to go towards equilibrium.

The Nernst Electrode Equation. We have seen that the difference in potential between a metal and a solution of its ions in which it is placed is related to the electrolytic solution pressure of the metal and the osmotic pressure of the solution. On the basis of theoretical considerations, Nernst developed the following equation which provides a qualitative interpretation of electrode potentials, but it cannot be tested quantitatively because the absolute values of E and P are not known:

$$E = \frac{RT}{nF} \ln \frac{p}{P}$$

E = potential difference, expressed in volts, between the metal and its ions.
R = the gas constant = 8.315 joules per degree.
T = absolute temperature.
n = valence change of the metal.
F = the faraday, i.e., the quantity of electricity associated with 1 gram-equivalent = 96,500 coulombs.
ln = the natural logarithm to the base e.
p = osmotic pressure of the solution.
P = electrolytic solution pressure of the metal.

By substituting in the equation the values for R and F and converting natural logarithms into common logarithms by multiplying by 2.303, we get

$$E = \frac{0.000198T}{n} \log \frac{p}{P}$$

For 25° C. or 298° A., the equation is

$$E = \frac{0.059}{n} \log \frac{p}{P}$$

We may substitute the equilibrium concentration of ions, k, for the electrolytic solution pressure, P, and may express p in terms of the ionic concentration, C, since osmotic pressure is proportional to the concentration of the ions. The equation then becomes

$$E = \frac{0.059}{n} \log \frac{C}{k}$$

Reference Electrodes. The potential difference at the contact of a metal and a solution of its ions cannot be measured directly. However, its relative value can be obtained by forming a galvanic cell in which one electrode is arbitrarily taken as the standard or reference electrode and the other electrode the one whose potential is to be measured. Since the absolute potential of a single electrode is not known, an arbitrary value is assigned to the reference electrode. The **normal hydrogen electrode** is now generally accepted as the standard, with an assigned potential of zero. This electrode consists of a strip of platinum (coated with platinum black) partly immersed in a solution of hydrochloric acid which is normal with respect to hydrogen ion, that is, a solution with an **effective** concentration of 1 gram-ion of hydrogen ions per 1000 grams of water. Better stated, the hydrochloric acid solution has unit activity. Hydrogen gas at 1 atmosphere pressure is constantly passed over the electrode and escapes through the openings at the bottom of the tube, as shown in Fig. 22. Thus the surface of the platinum is kept saturated with hydrogen gas. The coating of platinum black is deposited electrolytically. Platinum thus deposited is extremely finely divided, and in this state it has the property of condensing on its surface a large quantity of hydrogen and hence acts as

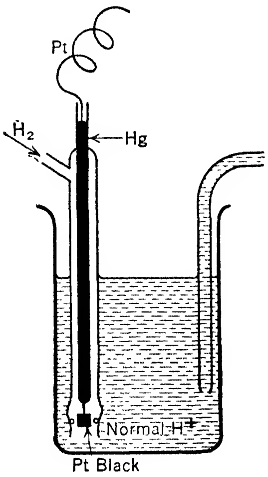

FIG. 22

though it were entirely hydrogen, i.e., it acts as an electrode of hydrogen.

By combining any half-cell with the hydrogen electrode and measuring the voltage of the whole cell with a sensitive voltmeter or potentiometer, the potential of the half-cell is obtained in terms of the arbitrary zero of potential.

Another standard electrode frequently used is the **normal calomel electrode.** This electrode is more convenient to use than the hydrogen electrode, and by careful experimental measurements its potential has been found to be +0.281 volt at 25° C. That is to say, the normal calomel electrode is 0.281 volt more positive than the normal hydrogen electrode. A calomel electrode is shown diagrammatically in Fig. 23. It consists of a glass tube containing a little mercury covered by a layer of calomel paste (a mixture of Hg_2Cl_2 and Hg) and the latter covered with a solution of potassium chloride saturated with mercurous chloride. A platinum wire (*A*) previously sealed into the bottom of the glass tube serves to connect the mercury with the external circuit. The side-tube *B* is filled with potassium chloride solution by applying suction at side-tube *C*. The latter is then closed by means of a clamp. Side-tube (*B*) dips into an intermediate vessel which contains a solution of potassium chloride and into which also dips the side-arm of the half-cell whose potential is desired. Thus the potential E_0 of any half-cell may be easily determined in terms of the arbitrary zero of potential E_1 by simply combining it with a calomel electrode and measuring the voltage *E* of the whole cell with a potentiometer or sensitive voltmeter. That is to say, the voltage *E* of this galvanic cell is a direct measure of the single electrode potential E_0, because the single electrode potential E_1 of the normal hydrogen electrode is taken as zero.[3]

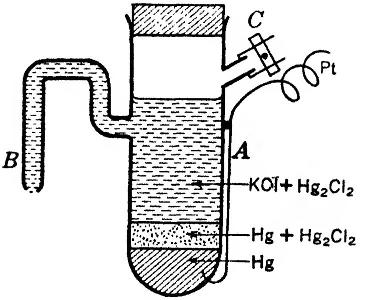

FIG. 23

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[3] The signs given to cell potentials and electrode potentials depend upon the conventions which are adopted. According to common practice in America, the equation for the above cell may be written: $E = E_1 + E_0$.

The potassium chloride solution in the calomel cell may be normal, tenth-normal, or saturated. The potentials of these electrodes at 25° C. are +0.281, +0.336, and +0.246 volt, respectively, when referred to the normal hydrogen electrode as the standard.

Case 34. Calculation of the Relative Equilibrium Concentration of Ions.

If a rod or strip of metal, for example, copper, be immersed in a solution of its ions and connected with a normal hydrogen electrode by means of a "salt bridge," upon connecting the two poles of the cell an e.m.f. develops. Such a cell is illustrated in Fig. 24. Since the potential difference of the normal hydrogen electrode has been given the arbitrary value of zero, the potential of the cell is taken as the single potential, E_0, of the metal electrode. Substituting this value in the Nernst equation, we can calculate the relative equilibrium ion concentration, also called the solution pressure constant.

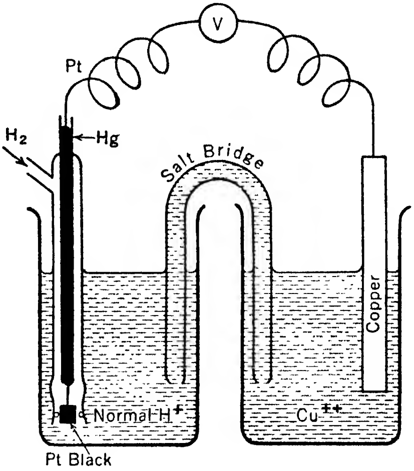

Fig. 24

Example 1. A strip of copper in equilibrium with a 1 M solution of its ions is connected with the normal hydrogen electrode, and the e.m.f. of the cell is found to be +0.34 volt at 25° C. Calculate $k_{\mathrm{Cu}^{++}}$.

This cell may be written as follows:

$$\mathrm{H_2(Pt)} \mid \mathrm{H^+}(1\,M) \parallel \mathrm{Cu^{++}}(1\,M) \mid \mathrm{Cu}$$ [4]

In this equation, the order in which the electrolyte ~~and~~ electrode are written is the same as they occur in the actual cell, i.e., (electrode, electrolyte) + (electrolyte, electrode). If both are written (electrode, electrolyte), then the equation becomes $E = E_1 - E_0$. When negative electricity flows inside the cell from right to left, the voltage of the cell is arbitrarily taken as positive, and *vice versa*.

[4] || indicates the elimination of the junction potential between solutions by means of a "salt bridge."

The Nernst equation is

$$E_{0(\mathrm{Cu})} = \frac{0.059}{n} \log \frac{C_{\mathrm{Cu}^{++}}}{k_{\mathrm{Cu}^{++}}}$$

E_0 for Cu = +0.34 and $C_{\mathrm{Cu}^{++}} = 1$. Substituting in the equation

$$+0.34 = \frac{0.059}{2} \log \frac{1}{k_{\mathrm{Cu}^{++}}}$$

$$\log \frac{1}{k_{\mathrm{Cu}^{++}}} = \frac{0.34}{0.0295} = 11.53$$

$$\log k_{\mathrm{Cu}^{++}} = -11.53 \text{ or } \overline{12}.47$$

$$k_{\mathrm{Cu}^{++}} = 3 \times 10^{-12} \text{ gram-ion per liter}$$

The value of the solution pressure constant for copper is very small and indicates that cupric ions are easily transformed into metallic copper. It should be remembered that this value is purely relative and is based upon the arbitrary value of zero taken as the potential of the normal hydrogen electrode.

Example 2. The standard potential E_0 for zinc is −0.76 volt at 25° C. Calculate the solution pressure constant $k_{\mathrm{Zn}^{++}}$ for zinc.

The value for E_0 was obtained by measuring the e.m.f. of the following cell:

$$\mathrm{H_2(Pt)} \mid \mathrm{H^+}(1\,M) \parallel \mathrm{Zn^{++}}(1\,M) \mid \mathrm{Zn}$$

Substituting the value for E_0 in the Nernst equation, we get

$$-0.76 = \frac{0.059}{2} \log \frac{1}{k_{\mathrm{Zn}^{++}}}$$

$$\log \frac{1}{k_{\mathrm{Zn}^{++}}} = \frac{-0.76}{0.0295} = -25.76$$

$$\log k_{\mathrm{Zn}^{++}} = 25.76$$

$$k_{\mathrm{Zn}^{++}} = 6 \times 10^{25} \text{ gram-ions per liter}$$

Such an enormous value (10^{25}) for the concentration of Zn^{++} ions in a solution cannot be obtained with any known zinc salt. However, it must be remembered that all k values are relative and depend upon the arbitrary value of zero assigned to the normal hydrogen electrode. The enormous value for zinc simply means that the tendency for zinc to form ions is very great.

Normal or Standard Electrode Potentials. As explained in the preceding pages, the potential at the contact between a metal and a solution of its ions is a measure of the tendency of the metal to detach electrons and go into solution in the form of ions.

This electrode potential varies with the concentration of the solution and hence it is necessary to adopt some standard concentration. The **normal electrode potential,** also called the molar or standard electrode potential, is defined as the potential set up by a metal dipped into a solution of its ions at unit activity, that is, a solution which contains an effective ion concentration of 1 gram-ion per 1000 grams of solvent. Since the normal electrode potential is referred to the normal hydrogen electrode chosen as standard and given an arbitrary value of zero, it is a relative potential. In order to indicate whether the metal is positive with reference to the hydrogen electrode, i.e., will plate out, or negative, i.e., will dissolve and thus displace hydrogen, the single potential is given the sign of the metal. The normal or standard electrode potential is obtained from a cell of the following type:

$$\mathrm{Pt(H_2)} \mid \mathrm{H^+ \text{ ion }} (1\,M) \parallel M^+ \,(1\,M) \mid M$$

The arrangement of such a cell is shown diagrammatically in Fig. 24.

Case 35. Calculation of Electrode Potentials.

The potential difference between a metal and a solution of its ions, referred to the normal hydrogen electrode taken as zero, may be calculated from the Nernst equation (see page 221).

$$E = \frac{0.059}{n} \log \frac{C}{k} \tag{1}$$

$$= \frac{0.059}{n} \log C + \frac{0.059}{n} \log \frac{1}{k} \tag{2}$$

When the concentration, C, of the metal ion is 1 M, the potential becomes the molar electrode potential, E_0, and since $\log 1 = 0$, the equation reduces to

$$E_0 = \frac{0.059}{n} \log \frac{1}{k}$$

Substituting E_0 for $\frac{0.059}{n} \log \frac{1}{k}$ in equation (2), we have

$$E = E_0 + \frac{0.059}{n} \log C \tag{3}$$

By measuring E, the e.m.f. of a cell, such as is illustrated in Fig. 24, and substituting its value in equation (3), we can calculate the molar or standard potential E_0. The value of E_0 being known, the value of the potential at any concentration can be calculated with the aid of equation (3).

Values of E_0 for a number of the elements are given in Table XIII, which is the well-known electromotive series of the metals. The metals thus arranged show a decreasing tendency to become oxidized, i.e., they become poorer reducing agents, while their ions become more effective oxidizing agents, as you go down the table. In other words, any metal will reduce the ions of all metals below it in the potential series, i.e., will displace these metals from solution. For example, iron will displace copper, copper will displace mercury, and so on.

TABLE XIII

STANDARD ELECTRODE POTENTIALS AT 25°

Electrode	Half-Cell Reaction	E_0 (Normal Hydrogen Electrode = 0)
Li^+, Li	$Li^+ + e \rightleftharpoons Li$	−2.960
K^+, K	$K^+ + e \rightleftharpoons K$	−2.924
Ca^{++}, Ca	$Ca^{++} + 2e \rightleftharpoons Ca$	−2.76
Na^+, Na	$Na^+ + e \rightleftharpoons Na$	−2.715
Mg^{++}, Mg	$Mg^{++} + 2e \rightleftharpoons Mg$	−1.55
Zn^{++}, Zn	$Zn^{++} + 2e \rightleftharpoons Zn$	−0.762
Fe^{++}, Fe	$Fe^{++} + 2e \rightleftharpoons Fe$	−0.441
Cd^{++}, Cd	$Cd^{++} + 2e \rightleftharpoons Cd$	−0.401
Co^{++}, Co	$Co^{++} + 2e \rightleftharpoons Co$	−0.29
Ni^{++}, Ni	$Ni^{++} + 2e \rightleftharpoons Ni$	−0.22
Sn^{++}, Sn	$Sn^{++} + 2e \rightleftharpoons Sn$	−0.136
Pb^{++}, Pb	$Pb^{++} + 2e \rightleftharpoons Pb$	−0.122
$(H^+, H_2)Pt$	$H^+ + e \rightleftharpoons \frac{1}{2}H_2$	0.000
Cu^{++}, Cu	$Cu^{++} + 2e \rightleftharpoons Cu$	+0.344
$(I^-, I_2)Pt$	$\frac{1}{2}I_2 + e \rightleftharpoons I^-$	+0.535
Ag^+, Ag	$Ag^+ + e \rightleftharpoons Ag$	+0.799
Hg_2^{++}, Hg	$Hg^{++} + 2e \rightleftharpoons 2Hg$	+0.799
$(Br^-, Br_2)Pt$	$\frac{1}{2}Br_2 + e \rightleftharpoons Br^-$	+1.065
$(Cl^-, Cl_2)Pt$	$\frac{1}{2}Cl_2 + e \rightleftharpoons Cl^-$	+1.358
Au^{+++}, Au	$Au^{+++} + 3e \rightleftharpoons Au$	+1.38
$(F^-, F_2)Pt$	$\frac{1}{2}F_2 + e \rightleftharpoons F^-$	+1.96

Case 36. Calculation of the E.M.F. of a Cell.

The e.m.f. of any cell is obtained by calculating the potential difference, E, at each electrode and then taking the algebraic difference.

Example. Calculate the e.m.f. of the following Daniell cell:

$$\mathrm{Zn} \mid \mathrm{Zn}^{++}(0.1\ M) \parallel \mathrm{Cu}^{++}(0.001\ M) \mid \mathrm{Cu}$$

$$E_{0_{\mathrm{Zinc}}} = -0.76 \text{ and } E_{0_{\mathrm{Copper}}} = +0.34.$$

Substituting the values of E_0 for zinc and copper, respectively, we have:
For zinc,

$$\begin{aligned} E &= -0.76 + \frac{0.059}{2} \log 0.1 \\ &= -0.76 + (0.0295 \times -1) \\ &= -0.76 - 0.0295 = -0.79 \text{ volt} \end{aligned}$$

For copper,

$$\begin{aligned} E &= +0.34 + \frac{0.059}{2} \log 0.001 \\ &= +0.34 + (0.0295 \times -3) \\ &= +0.34 - 0.09 = +0.25 \text{ volt} \end{aligned}$$

$\therefore$ The e.m.f. of the cell $= +0.25 - (-0.79) = 1.04$ volts.

Concentration Cells. In the above type of cell, illustrated by the Daniell cell, the electrodes consist of two different metals immersed into solutions of their respective ions. By using the same metal at each pole but immersing it in solutions of different concentrations, an electric current will flow when the two poles are connected. Such cells are called **concentration cells.** Denoting the metal by M, we may write such a cell as follows:

$$\underset{}{M} \mid \underset{C_1}{M^+ \text{ ion (dilute)}} \parallel \underset{C_2}{M^+ \text{ ion conc.}} \mid M$$

If E_1 and E_2 denote the pole potentials at concentrations C_1 and C_2, respectively, then by substituting in the Nernst equation we get

$$E_1 = \frac{0.059}{n} \log \frac{C_1}{k_1}$$

$$E_2 = \frac{0.059}{n} \log \frac{C_2}{k_2}$$

$$\therefore \quad \text{e.m.f.} = E_2 - E_1 = \frac{0.059}{n}\left(\log\frac{C_2}{k_2} - \log\frac{C_1}{k_1}\right)$$

$$= \frac{0.059}{n}\log\frac{C_2}{C_1}$$

Oxidation and Reduction Potentials. Oxidizing agents (oxidants) and reducing agents (reductants) have already been discussed (page 29). The oxidizing potential of an oxidant has been found by experiment to depend upon the logarithm of the ratio of the concentrations of the oxidized and reduced forms. Likewise, the reduction potential is dependent upon this same logarithmic ratio, being numerically the same as the oxidizing potential **but with the sign reversed.** In order to compare the oxidizing potentials of various oxidizing agents, it is necessary to adopt some uniform ratio of the concentration of the oxidized to the reduced form. The value of this ratio has been taken as 1. In other words, the potentials are determined for solutions containing equal concentrations of the oxidized and reduced forms of the oxidant. When the potential of such a solution is measured against the normal hydrogen electrode taken as zero, it is termed the **standard oxidizing potential.** In Table XIV a few **standard reduction potentials** are recorded. By changing the sign of the values of E_0, the standard oxidizing potentials are obtained for the respective half-cell reactions.

TABLE XIV

STANDARD REDUCTION POTENTIALS AT 25°

Electrode	Half-Cell Reaction	E_0 (Normal Hydrogen Electrode = 0)
$(Sn^{++++}, Sn^{++})Pt$	$Sn^{++++} + 2e \rightleftharpoons Sn^{++}$	+0.13
$(Fe^{+++}, Fe^{++})Pt$	$Fe^{+++} + e \rightleftharpoons Fe^{++}$	+0.75
$(Hg^{++}, Hg_2^{++})Pt$	$Hg^{++} + e \rightleftharpoons \frac{1}{2}Hg_2^{++}$	+0.90
$(MnO_4^-, Mn^{++})Pt$	$MnO_4^- + 8H^+ + 5e \rightleftharpoons Mn^{++} + 4H_2O$	+1.48
$(Ce^{++++}, Ce^{+++})Pt$	$Ce^{++++} + e \rightleftharpoons Ce^{+++}$	+1.55
$(Cr^{+++}, Cr^{++})Pt$	$Cr^{+++} + e \rightleftharpoons Cr^{++}$	−0.40
$(I^-, I_2)Pt$	$I^- \rightleftharpoons \frac{1}{2}I_2 + e$	−0.54
$(Br^-, Br_2)Pt$	$Br^- \rightleftharpoons \frac{1}{2}Br_2 + e$	−1.07
$(Cl^-, Cl_2)Pt$	$Cl^- \rightleftharpoons \frac{1}{2}Cl_2 + e$	−1.36

If we denote the concentrations of the oxidized and reduced forms of the oxidant by $C_{\text{ox.}}$ and $C_{\text{red.}}$, respectively, and let $E_{(\text{ox-red.})}$ denote the difference in potential developed in going from a higher to a lower valence, it can be shown that

$$E_{(\text{ox-red.})} = \frac{0.059}{n} \log \frac{C_{\text{ox.}}}{C_{\text{red.}} \times C_K}$$

where K is the value of the ratio $\frac{C_{\text{ox.}}}{C_{\text{red.}}}$ at equilibrium.

Case 37. Calculation of the Equilibrium Constant for Oxidation-Reduction Reactions.

Oxidation-reduction reactions are reversible and consequently obey the law of chemical equilibrium. That is to say, such reactions proceed in a given direction until equilibrium is established. The displacement of one metal from solution by another is a simple example of oxidation and reduction. For instance, a rod of zinc dipped in a solution of copper sulfate will plate out metallic copper and at the same time Zn^{++} ions will go into solution. Or in the Daniell cell, when the two poles are connected, zinc is oxidized in one compartment and simultaneously Cu^{++} ions are reduced in the other. A current will continue to flow so long as there is a difference in potential of the two poles. When the difference in potential reaches zero, i.e., when equilibrium is reached, the current stops. The reaction is represented by the following equation:

$$\underset{\substack{\text{Reducing}\\\text{agent}}}{Zn^\circ} + \underset{\substack{\text{Oxidizing}\\\text{agent}}}{Cu^{++}} \rightleftharpoons Zn^{++} + Cu^\circ$$

Applying the law of chemical equilibrium, we have

$$\frac{C_{Zn^{++}} \times C_{Cu^\circ}}{C_{Zn^\circ} \times C_{Cu^{++}}} = K$$

But since Cu° and Zn° are solids, the values of C_{Cu° and C_{Zn} will be constant. Hence, the equation reduces to

$$\frac{C_{Zn^{++}}}{C_{Cu^{++}}} = K$$

where K is the equilibrium constant. Its value may be calculated with the aid of the Nernst equation. Thus, for zinc in equilibrium with Zn^{++} ions, we have

$$E_{\text{zinc}} = E_{0_{\text{zinc}}} + \frac{0.059}{2} \log C_{\text{Zn}^{++}} \tag{1}$$

Similarly, with the copper electrode we get

$$E_{\text{copper}} = E_{0_{\text{copper}}} + \frac{0.059}{2} \log C_{\text{Cu}^{++}} \tag{2}$$

At equilibrium $E_{\text{zinc}} = E_{\text{copper}}$; $E_{0_{\text{zinc}}} = -0.76$ and $E_{0_{\text{copper}}} = 0.34$. Substituting these values and equating equations (1) and (2) we get

$$-0.76 + 0.0295 \log C_{\text{Zn}^{++}} = \underline{0.0295 \log} \text{ Cu}^{++} + 0.34$$

$$0.0295 (\log C_{\text{Zn}^{++}} - \log C_{\text{Cu}^{++}}) = 1.10$$

$$\log \frac{C_{\text{Zn}^{++}}}{C_{\text{Cu}^{++}}} = 37.3$$

$$\frac{C_{\text{Zn}^{++}}}{C_{\text{Cu}^{++}}} = K = 1 \times 10^{37.3} = 2 \times 10^{37}$$

Hence, equilibrium will not be reached until the concentration of Zn^{++} ions is 2×10^{37} times greater than the Cu^{++} ion concentration. This means that copper is practically completely precipitated from its solution by zinc. If the $\frac{C_{\text{Zn}^{++}}}{C_{\text{Cu}^{++}}}$ ratio of a solution is less than 10^{37} and a piece of zinc is added, then Zn^{++} ions will go into solution until the ratio equals 10^{37}. If the $\frac{C_{\text{Zn}^{++}}}{C_{\text{Cu}^{++}}}$ ratio is greater than 10^{37}, no zinc goes into solution; but if a piece of copper is added, then Cu^{++} ions pass into solution and zinc plates out until the ion concentration ratio becomes 10^{37}. In other words, the current will flow in the reverse direction.

The value for K can also be calculated from the solution pressure constants for zinc and copper, k_{Zn} and k_{Cu}, respectively. On page 224 these values were calculated to be $k_{\text{Zn}} = 6 \times 10^{25}$ and $k_{\text{Cu}} = 3 \times 10^{-12}$.

The electrode potentials of the above cell are:

$$E_{\mathrm{Zn}} = \frac{0.059}{2} \log \frac{C_{\mathrm{Zn}^{++}}}{k_{\mathrm{Zn}}}$$

$$E_{\mathrm{Cu}} = \frac{0.059}{2} \log \frac{C_{\mathrm{Cu}^{++}}}{k_{\mathrm{Cu}}}$$

At equilibrium $E_{\mathrm{Zn}} = E_{\mathrm{Cu}}$ and hence

$$\frac{0.059}{2} \log \frac{C_{\mathrm{Zn}^{++}}}{k_{\mathrm{Zn}}} = \frac{0.059}{2} \log \frac{C_{\mathrm{Cu}^{++}}}{k_{\mathrm{Cu}}}$$

$$\log \frac{C_{\mathrm{Zn}^{++}}}{k_{\mathrm{Zn}}} = \log \frac{C_{\mathrm{Cu}^{++}}}{k_{\mathrm{Cu}}}$$

$$\frac{C_{\mathrm{Zn}^{++}}}{C_{\mathrm{Cu}^{++}}} = \frac{k_{\mathrm{Zn}}}{k_{\mathrm{Cu}}} = K$$

Substituting the values of k_{Zn} and k_{Cu}, we get

$$\frac{C_{\mathrm{Zn}^{++}}}{C_{\mathrm{Cu}^{++}}} = \frac{6 \times 10^{25}}{3 \times 10^{-12}} = K = 2 \times 10^{37}$$

Suppose that we take another oxidation-reduction reaction, for example, the action of chlorine on ferrous ions. The reversible reaction is written as follows:

$$2\mathrm{Fe}^{++} + \mathrm{Cl}_2 \rightleftharpoons 2\mathrm{Fe}^{+++} + 2\mathrm{Cl}^-$$

Applying the law of chemical equilibrium, we have

$$\frac{C^2_{\mathrm{Fe}^{+++}} \times C^2_{\mathrm{Cl}^-}}{C^2_{\mathrm{Fe}^{++}} \times C_{\mathrm{Cl}_2}} = K$$

In a voltaic cell, one electrode would be the ferrous-ferric system and the other the chlorine-chloride system. Upon connecting the two systems, equilibrium will be attained when the total voltage of the cell becomes zero. At equilibrium,

$$E_{0(\mathrm{Fe}^{++},\,\mathrm{Fe}^{+++})} + \frac{0.059}{n} \log \frac{C_{\mathrm{Fe}^{+++}}}{C_{\mathrm{Fe}^{++}}} = E_{0(\mathrm{Cl}_2,\mathrm{Cl}^-)} + \frac{0.059}{n} \log \frac{C_{\mathrm{Cl}_2}}{C^2_{\mathrm{Cl}^-}}$$

In Table XIV the standard potential for the reversible reaction $\mathrm{Fe}^{+++} + e \rightleftharpoons \mathrm{Fe}^{++}$ at 25° C. is +0.75 volt, and for

$Cl_2 + 2e \rightleftharpoons 2Cl^-$ it is +1.36 volt. Substituting these values, we get

$$0.75 + \frac{0.059}{2} \log \frac{C^2_{Fe^{+++}}}{C^2_{Fe^{++}}} = 1.36 + \frac{0.059}{2} \log \frac{C_{Cl_2}}{C^2_{Cl^-}}$$

$$\frac{0.059}{2} \log \frac{C^2_{Fe^{+++}}}{C^2_{Fe^{++}}} - \frac{0.059}{2} \log \frac{C_{Cl_2}}{C^2_{Cl^-}} = 1.36 - 0.75 = +\ 0.61$$

$$\frac{0.059}{2} \log \frac{C^2_{Fe^{+++}} \times C^2_{Cl^-}}{C^2_{Fe^{++}} \times C_{Cl_2}} = +\ 0.61$$

$$\log \frac{C^2_{Fe^{+++}} \times C^2_{Cl^-}}{C^2_{Fe^{++}} \times C_{Cl_2}} = 20.68 = \log K$$

$$\therefore \quad K = 4.8 \times 10^{20}$$

This large value for K shows that the reaction $2Fe^{++} + Cl_2 \rightleftharpoons 2Fe^{+++} + 2Cl^-$ runs far towards completion, from left to right.

PROBLEMS

1. Calculate the relative equilibrium ion concentration (solution pressure constant) for silver. The half-cell reaction is $Ag^+ + e \rightleftharpoons Ag^\circ$, and the molar potential is +0.80 volt at 25° C.

Ans. 2.8×10^{-14}.

2. What are the values of the solution pressure constants for iron in the following half-cell reactions: (*a*) $Fe^{++} + 2e \rightleftharpoons Fe^\circ$, and (*b*) $Fe^{+++} + 3e \rightleftharpoons Fe^\circ$? The standard electrode potential for (*a*) is −0.44 volt and for (*b*) is −0.04 volt at 25° C.

Ans. (*a*) 8.3×10^{14}.
(*b*) 1.1×10^{2}.

3. The normal electrode potential for bromine is +1.07 volt at 25° C. Calculate its solution pressure constant.

Ans. 5.4×10^{-37}.

4. Calculate the solution pressure constants for the following half-cell reactions: (*a*) $Li^+ + e \rightleftharpoons Li^\circ$, (*b*) $Sn^{++} + 2e \rightleftharpoons Sn^\circ$, and (*c*) $Hg_2^{++} + 2e \rightleftharpoons 2Hg^\circ$. The molar or normal electrode potentials at 25° C. are: (*a*) −2.96 volts, (*b*) −0.14 volt, and (*c*) +0.80 volt.

Ans. (*a*) 1.6×10^{50}.
(*b*) 5.6×10^{4}.
(*c*) 7.6×10^{-28}.

5. Iron displaces copper from solutions of copper salts according to the reaction:

$$Cu^{++} + Fe^\circ \rightleftharpoons Cu^\circ + Fe^{++}$$

The molar potential for iron is -0.44 volt and for copper $+0.34$ volt at 25° C. Calculate the equilibrium constant for the reaction.

Ans. 2.8×10^{26}.

6. The solution pressure constant for zinc is 6×10^{25} and for mercury 8×10^{-28}. Calculate the equilibrium constant for the reaction in which metallic zinc displaces mercury from solution.

$$Zn^\circ + Hg^{++} \rightleftharpoons Zn^{++} + Hg^\circ$$

Ans. 7.5×10^{52}.

7. Calculate the e.m.f. of the following Daniell cell:

$$Zn \mid Zn^{++}(0.001\ M) \parallel Cu^{++}(0.01\ M) \mid Cu$$
$$E_{0_{\text{zinc}}} = -\ 0.76 \text{ and } E_{0_{\text{copper}}} = +\ 0.34$$

Ans. 1.13 volt.

8. What is the e.m.f. of the following concentration cell?

$$Ag \mid Ag^+(0.01\ M) \parallel Ag^+(0.1\ M) \mid Ag$$

Ans. 0.059 volt.

9. Calculate the value of the equilibrium ratio $\frac{C_{Cl_2}}{C^2_{Cl^-}}$ for the half-cell reaction:

$$Cl^\circ_2 + 2e \rightleftharpoons 2Cl^-$$
$$E_0 = +\ 1.36 \text{ volt}$$

Ans. 7.9×10^{-47}.

10. The normal reduction potential of the following electrode reaction is $+0.75$ volt at 25° C.: $Fe^{+++} + e \rightleftharpoons Fe^{++}$. What is the value of the equilibrium ratio $\frac{C_{Fe^{+++}}}{C_{Fe^{++}}}$?

Ans. 1.95×10^{-13}.

11. Calculate the equilibrium constant for the reaction:

$$2Fe^{++} + I_2 \rightleftharpoons 2Fe^{+++} + 2I^-$$
$$E_{0(Fe^{+++},\ Fe^{++})} = +\ 0.75 \quad \text{and} \quad E_{0(I_2,\ I^-)} = +\ 0.54$$

Ans. 7.6×10^{-8}.

12. What is the equilibrium constant for the reaction:

$$Cl_2 + 2I^- \rightleftharpoons 2Cl^- + I_2?$$
$$E_{0_{\text{chlorine}}} = +\ 1.36 \quad \text{and} \quad E_{0_{\text{iodine}}} = +\ 0.54$$

Ans. 6.3×10^{27}.

13. Calculate the value of the equilibrium constant for the following oxidation-reduction reaction:

$$5Fe^{++} + MnO_4^- + 8H^+ \rightleftharpoons 5Fe^{+++} + Mn^{++} + 4H_2O$$
$$E_{0(Fe^{+++},\ Fe^{++})} = +\ 0.75 \quad \text{and} \quad E_{0(MnO_4^-,\ Mn^{++})} = +\ 1.5$$

Ans. 3.2×10^{63}.

14. Calculate the value of the equilibrium constant K for the following reversible reaction:

$$2\text{Fe}^{++} + \text{Cl}_2 \rightleftharpoons 2\text{Fe}^{+++} + 2\text{Cl}^-$$

$$k_{(\text{Fe}^{+++},\ \text{Fe}^{++})} = 1.3 \times 10^{-13} \quad \text{and} \quad k_{(\text{Cl}_2,\ \text{Cl}^-)} = 8 \times 10^{-47}$$

Ans. 2.1×10^{20}.

15. The equilibrium ratio $\dfrac{C_{\text{Zn}^{++}}}{C_{\text{Cu}^{++}}}$ in the Daniell cell is approximately 10^{37}; i.e., at this ratio the potential of the cell is zero. Suppose the following substances to be added in slight excess, and in succession, to the copper solution of the cell: NaOH, $(\text{NH}_4)_2\text{S}$, and KCN. Explain what would happen after the addition of each compound.

CHAPTER XX

CHEMICAL KINETICS

Up to this point we have considered the equilibrium established when the speeds of the forward and reverse reactions become equal. In the following paragraphs we shall consider the velocities of reactions and the intermediate steps taken in reaching the final results. The vast majority of inorganic reactions take place at such high rates that it is impossible to measure their velocities. Thus, in the neutralization of an acid by a base, the reaction is almost instantaneous. There are a few exceptions to this rule, for example, the decomposition of hydrogen peroxide and the oxidation of sulfur dioxide. These reactions proceed slowly enough to permit the measurement of their rates. In contrast with the reactions of inorganic chemistry, organic reactions are generally relatively slow. For example, the reaction between an alcohol and an acid to form an ester and water takes place very slowly at room temperature and its progress can be followed easily.

Reaction kinetics is concerned with the velocities of reactions, and with what happens during their courses. The problems of reaction kinetics are much more difficult and our knowledge is much less complete than in thermodynamics and its applications, where we are concerned only with the initial and final states of a system and not with what happens during the process. Often two or more reactions are taking place simultaneously, and sometimes the presence of a small quantity of impurity or catalyst has a pronounced effect upon the reaction velocity. Such factors make it difficult, if not impossible, to obtain consistent results experimentally. In a mixture of several organic substances, there may be a large number of different products thermodynamically possible but the predominating product will be the one produced by the fastest reaction. Hence it may be possible to obtain any desired one of several possible reactions by changing the concentrations or the temperature, or by adding a specific catalyst. Unless it is possible to cause the desired reaction to proceed much faster than all the other possible reactions, a low yield will be obtained. Another point to keep in mind is the fact that there is no apparent relation between reaction rate and chemical affinity. Certain reactions are so mild that only a few thousand calories of heat per mol are liberated in their courses, but the velocities are so high that they have not been measured. On the other hand, some reactions are so violent that they produce a great amount of heat and yet their reaction rates are immeasurably slow at ordinary temperatures in the absence of a catalyst.

The Order of Reactions. When only one molecule of a single substance undergoes change, the reaction is called **monomolecular,** or a **reaction of the first order,** and the rate of reaction is directly proportional to the concentration. When two molecules (of either the same or different species) react, the reaction is **dimolecular,** or a **reaction of the second order.** Correspondingly, we may have reactions of the third, fourth, or higher orders, although orders higher than the third are extremely rare. Each of these reaction orders may be treated mathematically, but space does not permit the reproduction of the equations here. The student is referred to a textbook on physical chemistry. Inspection of these equations shows that each of them contains a constant, k, which is called the **velocity constant,** or better, the **specific reaction rate** of the reaction in question. It should be pointed out that, if a reaction is allowed to proceed until equilibrium is reached, the equilibrium constant, K, derived for the mass action law equation, is determined by the ratio of the specific reaction rates of the forward and the reverse reactions (k_1 and k_2, respectively). The equilibrium constant, however, can tell nothing of the absolute velocities of the two separate reactions.

Monomolecular reactions are the simplest to treat mathematically, but they are much more difficult to explain chemically. The decomposition of nitrogen pentoxide into oxygen and a mixture of nitrogen dioxide and nitrogen tetroxide is a good example of a reaction of this type. The following equation represents the total reaction:

$$\begin{tikzcd} N_2O_5 \arrow[r] & 2NO_2 \arrow[d, shift left] & + \tfrac{1}{2}O_2 \\ & N_2O_4 \arrow[u, shift left] & \end{tikzcd}$$

The polymerization of the NO_2 to N_2O_4 does not affect the monomolecular character of the reaction as a whole because the velocity of the latter reaction, separately, is so great that it has never been measured.

Bimolecular reactions are by far the most common type; as an example, we shall consider the saponification of an ester by an alkali as represented by the equation,

$$CH_3COOC_2H_5 + NaOH \rightarrow CH_3COONa + C_2H_5OH$$

This reaction has been studied by several investigators. One of the interesting points is the fact that it is the **hydroxyl ion** rather than the NaOH molecule that is involved in the reaction. The proof is based upon the fact that, if a dilute solution of $Ba(OH)_2$ is used instead of NaOH, the rate of saponification still follows the bimolecular equation rather than the trimolecular equation, as would have been expected if the reaction involved the combination of a barium hydroxide molecule with two ethyl acetate molecules.

Only a few trimolecular reactions are known, because they involve the simultaneous collision of three molecules, and collisions of this type are quite rare. An example of this type, however, is the reaction between ferric chloride and stannous chloride, since in dilute aqueous solution the equation representing the change can be written

$$2Fe^{+++} + Sn^{++} \rightarrow 2Fe^{++} + Sn^{++++}$$

involving the collision of three ions. As with a number of other trimolecular reactions, secondary reactions take place, and when the conditions are varied, the constancy of k is not very satisfactory.

Several methods are available for determining the reaction order. One method involves simply the substitution of the concentration data into the different velocity equations, and the one which gives a constant value for k throughout the course of the reaction is the one corresponding to the order of the particular reaction being investigated. The order may be determined graphically by observing which of the following functions of the concentration, c, gives a straight line when plotted against the time, t:

1. Log c vs. t—Monomolecular reaction.
2. $1/c$ vs. t—Bimolecular reaction.
3. $1/c^2$ vs. t—Trimolecular reaction.

Many reactions are observed to follow the monomolecular equation when in reality they are not truly monomolecular. Such reactions are known as **pseudo-monomolecular** reactions. One example of a reaction of this type is the inversion of cane sugar, which takes place according to the following equation in the presence of a small amount of free acid:

$$C_{12}H_{22}O_{11} + H_2O \rightarrow \underset{\text{Fructose}}{C_6H_{12}O_6} + \underset{\text{Glucose}}{C_6H_{12}O_6}$$

This reaction is really bimolecular, and the water takes an active part; but since it is also the solvent, and therefore present in considerable excess, the amount used up in the course of the reaction does not appreciably change its concentration. If we started with a 0.5 *M* solution of cane sugar, the concentration of the water is reduced less than one per cent when the reaction is complete. The bimolecular equation reduces to the monomolecular equation when the concentration of one of the reactants is constant, and therefore this reaction follows the monomolecular equation quite closely.

Another pseudo-monomolecular reaction is the decomposition of hydrogen peroxide. Hydrogen peroxide is fairly stable when it is protected from contamination, but decomposes rapidly upon the addition of a small amount of some such substance as ferric chloride. Although this reaction also involves two substances, the ferric chloride is not used up in the reaction, and at the end just as much of it is present as at the beginning. In other words, the concentration of the ferric chloride remains constant and the reaction appears to follow the monomolecular law, the rate depending only upon the concentration of the hydrogen peroxide. Reactions of this type are called **catalytic reactions,** and the ferric chloride is called a **catalyst.** In the inversion of cane sugar, the small amount of free acid, or rather the hydrogen ion, acts as a catalyst for the reaction. It may be well to emphasize here the difference between the function of a catalyst and that of the water in the inversion of cane sugar. The concentration of the water remains practically constant because it is present in large excess. Only a small amount of catalyst need be used, and its concentration remains constant because it is actually used over and over again and remains unchanged at the end of the reaction.

Catalysts. A catalyst may be defined as a substance which changes the velocity of a chemical reaction but which itself remains unchanged when the reaction is complete. The process of changing reaction rates is called catalysis. Catalysts may be either **positive catalysts** or **negative catalysts,** depending on whether they increase or decrease the reaction rate. Most catalysts increase the rate and are called simply "catalysts." It must be remembered that a catalyst cannot shift the equilibrium point of a reaction. The catalyst accelerates the reverse reaction to the same extent as the forward reaction, so that their ratio, the equilibrium constant, remains unchanged. Moreover, a catalyst cannot initiate a reaction; it can only change the speed with which equilibrium is attained.

A special kind of catalysis, called **contact catalysis,** involves the adsorption on the surface of a solid of molecules from the gaseous phase or from solution. Molecules thus adsorbed are often (but not always) in a very reactive state, and there is opportunity for the formation of new products. Catalytic reactions at surfaces generally involve adsorption, although the converse is not necessarily true. The rates of catalytic reactions at surfaces depend principally upon the fraction of the surface that is covered by the adsorbed molecules. With gases, for instance, if the surface is nearly bare, the partial pressure or concentration of the gas determines the extent of adsorption, and in turn the rate of reaction. Since the rate depends upon the concentration, such reactions follow the monomolecular law and are of the first order. If the surface becomes practically "saturated," however, increasing the pressure cannot cause more molecules to come in contact with the surface, and the rate becomes independent of the pressure. Such reactions are said to be of "zero order."

Another special type of catalysis is known as **auto-catalysis.** Usually, of course, a given reaction starts out at the maximum rate and proceeds more and more slowly as the concentrations of the reactants decrease. Sometimes, however, one of the products may catalyze the reaction and temporarily increase the rate. Such a substance is called an **auto-catalyst,** and the rates of such reactions increase for a time during the early course of the reaction, pass through a maximum, and then gradually decrease.

Catalysts have many applications in industrial chemistry. Several may be mentioned: the Haber process for the synthesis of ammonia from hydrogen and atmospheric nitrogen; the synthesis of methanol from carbon monoxide and hydrogen; Sabatier's hydrogenation and dehydrogenation processes; and the removal of carbon monoxide from air by "Hopcalite," a catalytic mixture of certain metallic oxides.

CHAPTER XXI

THERMOCHEMISTRY, ELECTROCHEMISTRY, AND PHOTOCHEMISTRY

THERMOCHEMISTRY

Most chemical reactions are accompanied by a thermal change. Generally, heat is evolved. Such reactions are called **exothermic.** A few chemical changes take place with an absorption of heat and are termed **endothermic** reactions. Chemical reactions unaccompanied by any thermal change are indeed very rare and are almost entirely confined to the reciprocal transformations of optical isomers. Thermochemistry deals with the thermal changes accompanying chemical reactions.

Heat is a form of energy and hence may be resolved into two factors: an intensity factor (temperature) and a capacity factor (heat capacity). The product of these two factors is the **thermal energy,** which may be measured in any one of several units. A few of the most frequently employed thermal units are: the **small** calories (cal.), the quantity of heat required to raise the temperature of 1 gram of water from 15° to 16° C.; the **large** or **kilogram** calorie (Cal.), the quantity of heat required to raise 1000 grams of water from 15° to 16° C.; the joule (j.), a unit based on the c.g.s. system which is equal to 10^7 ergs; and the kilojoule (J.), equal to 10^{10} ergs. These different thermal units are related as follows:

$$1 \text{ cal.} = 0.001 \text{ Cal.} = 4.185 \text{ j.} = 0.004185 \text{ J.}$$

Thermochemical equations or energy equations express not only the quantitative chemical weight relations but also the increase in heat constant (ΔH) in passing from the reactants at the left of the equation to the reaction products on the right. For example,

$$\underset{12\text{ g.}}{C(s)} + \underset{32\text{ g.}}{O_2(g)} = \underset{44\text{ g.}}{CO_2(g)} \quad \Delta H = -94{,}400 \text{ cal.}$$

This equation indicates that 12 g. of solid carbon and 32 g. of gaseous oxygen contain 94,400 cal. more energy than does 44 g. of gaseous carbon dioxide, at the same temperature. In writing energy equations, it is necessary to designate the state of aggregation of the reactants and resultants, since the energy content of a substance is not the same in the gaseous (*g*), liquid (*l*), and solid (*s*) states. The heat changes accompanying chemical reactions are measured in an apparatus called a *calorimeter.*

Laws of Lavoisier and Laplace, and of Hess. The first law of thermochemistry was enunciated by Lavoisier and Laplace in 1780 and states that **the quantity of heat required to decompose a chemical compound is exactly equal to the heat evolved when the compound is formed from its elements.** This law is a direct corollary of the law of the conservation of energy, or the first law of thermodynamics, which was clearly formulated by Mayer in 1842.

The second law of thermochemistry, discovered by Hess in 1840, states that **the heat evolved in a chemical process is the same regardless of the number of steps taken. It is called the law of constant heat summation.**

Heat of Formation. So far it has not been possible to determine the absolute heat contents of chemical compounds, but their **heats of formation** can be calculated by assuming that the heat content of each element is zero when in the standard state. Thus, the heat of formation (ΔH) of carbon dioxide is $-94{,}400$, since 94,400 cal. of heat is evolved in the formation of 1 mol of the gas from its elements.

Heat of Solution. The thermal change which takes place when 1 mol of a substance is dissolved in a volume of solvent so large that subsequent dilution produces no further thermal change is called the **heat of solution.**

Heat of Hydration. The difference between the heat of solution of an anhydrous salt and that of its hydrate is called the **heat of hydration.**

Heat of Dilution. When a solution of a specific concentration is diluted, the heat evolved, or absorbed, per mol of solute is termed the **heat of dilution.**

Heat of Combustion. The heat evolved during the complete oxidation of unit mass (the mol, in physicochemical calculations) of a substance is called its **heat of combustion.**

Heat of Neutralization. When dilute solutions of strong acids and strong bases are mixed in equivalent amounts, the heat evolved is practically the same in each case, namely, 13,800 cal. According to the electrolytic dissociation theory, the neutralization of any strong acid by any strong base is due entirely to the combination of hydrogen and hydroxyl ions to form undissociated water. Hence, ΔH for the ionic reaction, $H^+ + OH^- \rightarrow H_2O$, is $-13{,}800$ cal. This is the heat of formation of water from its ions, and is termed the **heat of neutralization.** This must not be confused with the heat of formation of water from its elements, which is $-68{,}000$ cal.

ELECTROCHEMISTRY

The science of electrochemistry had its birth at the beginning of the nineteenth century when Volta discovered that electrical energy could be obtained from chemical energy. This he accomplished by an apparatus he devised, which was simply a pile of discs of zinc and silver placed alternately one above the other, the silver disc of one pair being separated from the zinc disc of the next pair by blotting paper soaked in brine. By connecting the top and bottom discs with wires, an electrical current was found to flow, sufficient to produce a shock when their ends were touched with moist fingers. Such an apparatus is called a voltaic or galvanic pile (battery). This was an epoch-making discovery, and shortly afterwards Nicholson and Carlisle (1800) decomposed water and Davy (1807) isolated the alkali metals electrically.

Electrical energy may be produced by various chemical reactions, which are all of one type, according to the electronic theory, namely, oxidation (loss of electrons) at one electrode and reduction (gain of electrons) at the other electrode.

In 1827 Ohm discovered an important law of electrical conductance. It is known as Ohm's law and may be stated thus: The electric current I is proportional to the voltage E and inversely proportional to the resistance R:

$$I = \frac{E}{R} \quad \text{or} \quad \text{Amperes} = \frac{\text{Volts}}{\text{Ohms}}$$

The **ampere** is the current of electricity which will deposit silver from a solution of silver nitrate at the rate of 0.001118 g. per second. The **volt** is the unit of intensity, or the potential difference between the electrodes (electromotive force, e.m.f.). The **ohm** is the unit of resistance. The **coulomb** is the unit quantity of electricity; it is the amount of electricity which passes when a current of 1 ampere flows for 1 second. The **faraday** (F.) is 96,500 coulombs and is the quantity of electricity carried by 1 gram-equivalent of any ion. This electrical unit was named for Faraday whose experimental study (1833–1834) of electrolysis led him to discover two fundamental laws of electrolysis. These laws may be stated thus: (1) The mass of any substance liberated at an electrode during electrolysis is proportional to the quantity of electricity passed through the electrolytic cell; (2) when the same quantity of electricity passes through different electrolytes, the masses of the substances liberated at the electrodes are proportional to their chemical equivalents.

Conductance. The **specific resistance** of a solution is the resistance in ohms of a centimeter cube of the solution. The **specific conductance** is the reciprocal of specific resistance; it is stated in reciprocal ohms (r.o.), or mhos, and is generally designated by the Greek letter κ. In practice, it is convenient to express conductance in terms of the equivalent concentration, since the conductance depends almost entirely upon the amount of solute present. The **equivalent conductance** [1] is the conductance (in reciprocal ohms) of a solution containing 1 gram-equivalent of solute held between two large flat electrodes 1 cm. apart and is generally designated by the Greek letter Λ. If V represents the volume of solution in cubic centimeters which contains 1 gram-equivalent of solute, then

$$\Lambda = \kappa V_e$$

Conductance measurements must be made at some definite and convenient temperature, since the numerical values vary with the temperature. As the concentration of a solution is decreased, its specific conductance decreases but its equivalent conductance

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[1] The **molar conductance,** designated by the Greek letter μ, was used by Ostwald and by H. C. Jones and his co-workers. It is defined as the conductance of a solution containing 1 gram-mol of solute held between two large flat electrodes, and its value may be obtained by multiplying the specific conductance, κ, by the number of liters (not cubic centimeters) required to contain 1 gram-mol of solute. The values of μ given by Ostwald and by Jones are based on the Siemens resistance unit and must be multiplied by 1.066 to reduce to reciprocal ohms.

increases at first and then approaches a limiting value called the equivalence conductance, Λ_∞, at infinite dilution.

Conductance and Ionization. We have already pointed out in discussing Arrhenius' electrolytic dissociation theory (page 80) that the conductance of solutions of electrolytes is due to the presence of ions which are the current carriers. If conductance is due to the ions alone and if maximum equivalent conductance means complete ionization, it is obvious that the ratio of the equivalent conductance Λ_v of an electrolyte solution at any given dilution v to its equivalent conductance Λ_∞ at "infinite" dilution is a measure of the degree of its ionization. Expressed mathematically,

$$\alpha = \frac{\Lambda_v}{\Lambda_\infty}$$

where α is the degree of dissociation or ionization. Multiplying α by 100 gives the percentage ionization.

This relationship is not strictly true, since the velocities of the ions have an effect on electrical conductance and ionic velocities are affected by concentration due to variation of the interionic attraction. However, the simple equation of Arrhenius is adequate for dilute solutions of weak electrolytes. Moreover, since there is no sharp dividing line between weak electrolytes and strong electrolytes, the equivalent conductance ratio serves as a convenient method of determining the approximate degree of ionization of electrolytes.

For strong electrolytes, the value of Λ_∞ may be found by extrapolating the conductance values obtained at finite concentrations down to 0.0001 M, when little or no apparent increase in conductance is observed. This method for obtaining Λ_∞ cannot be used with weak electrolytes on account of experimental difficulty in making accurate conductance measurements at concentrations below 0.0001 M. Fortunately, Kohlrausch has shown experimentally that the equivalent conductance Λ_∞ at infinite dilution of different electrolytes is equal to the sum of the conductances of the individual ions.

Let us examine the law of Kohlrausch. The conductivity of a solution of an electrolyte depends on three factors: (1) the number of ions between the electrodes, (2) the valence (i.e., number of charges), and (3) the velocity with which the ions move. For example, in a solution of NaCl the numbers of Na^+ ions and of Cl^- ions are equal, and the valences are also equal. However, the velocities of migration (mobilities) of Na^+ ions and of Cl^- ions are different. Their relative velocities have been observed. Since the numbers of Na^+ ions and of Cl^- ions and the valences are alike, the value of the conductance at infinite dilution can be divided between the ions. By stating the ionic velocities (relative) in the same unit as the ionic conductance, their sum will equal the equivalent conductance at infinite dilution. This relationship is known as **Kohlrausch's law** and may be expressed as follows:

$$\Lambda_\infty = \Lambda_b + \Lambda_a \tag{1}$$

where Λ_b and Λ_a are the equivalent conductances of the cation and anion, respectively, at infinite dilution.

At any given dilution v, the degree of ionization is α, and, hence, there will be present in the solution α equivalents of the cation and anion per gram equivalent of electrolyte. Therefore, the equivalent conductance of the solution will be:

$$\Lambda_v = \alpha(\Lambda_b + \Lambda_a) \tag{2}$$

By dividing equation (2) by (1) we obtain the Arrhenius equation for the value of α, namely

$$\alpha = \frac{\Lambda_v}{\Lambda_\infty} \tag{3}$$

Ionic conductances at infinite dilution and for various temperatures may be found in published tables, and, hence, in order to determine α of a given electrolyte, it is usually only necessary to measure its conductance, Λ_v, at any convenient temperature and then substitute in the Arrhenius equation. A few ionic conductances at infinite dilution and at 18° are given in the following table.

In addition to the determination of the degree of ionization of solutions of electrolytes, other important applications of conductance measurements are: (1) the determination of the dissociation of water; (2) measurement of the degree of hydrolysis of various salts; (3) estimation of the basicity of organic acids; (4) detection of end-points in various volumetric titrations (colored solutions, turbid solutions, neutralizations, precipitations, etc.); and (5) determination of the solubilities of slightly soluble salts.

TABLE XV

IONIC CONDUCTANCES AT INFINITE DILUTION

(Temperature 18°)

Cation	Λ_b	Anion	Λ_a
Li^+	33.0	Cl^-	65.3
Na^+	43.2	Br^-	67.4
K^+	64.3	I^-	66.3
Rb^+	67.6	ClO_3^-	54.9
Cs^+	67.5	IO_3^-	33.8
NH_4^+	64.5	NO_3^-	61.7
Tl^+	65.5	$C_2H_3O_2^-$	35.0
Ag^+	53.9	$\frac{1}{2}SO_4^{=}$	68.0
$\frac{1}{2}Zn^{++}$	45.6	$\frac{1}{2}CO_3^{=}$	70.0
$\frac{1}{2}Mg^{++}$	45.0	$\frac{1}{2}C_2O_4^{=}$	61.0
$\frac{1}{2}Ba^{++}$	55.0	OH^-	173.8
$\frac{1}{2}Pb^{++}$	61.0		
H^+	315.2		

The Electromotive Series of Metals. The electromotive series arranges the metals in the order of their activity. The alkali and alkaline earth metals are the most active and the noble metals the least. It is called the electromotive series because the order in which the metals are arranged can be determined with a high degree of accuracy by electromotive-force measurement of electrochemical cells. Hydrogen is taken as a reference standard. Although it is not a metal, yet it behaves chemically as a metal. It combines with non-metals and with non-metallic groups of atoms (radicals) to form acids. Any metal above hydrogen in the electromotive series will replace the acidic hydrogen atoms in the molecules of acids. In general, **any metal in the electromotive series will replace a metal below it from compounds of the latter,** and hence the series is often called the **replacement series** of the metals. For example, if an iron nail is placed in a solution of copper sulfate, copper is plated out on the nail and an equivalent amount of iron goes into solution as iron sulfate.

$$CuSO_4 + Fe \rightarrow FeSO_4 + Cu$$

Similarly, if a strip of copper is placed in a solution of silver nitrate, it becomes coated with pure silver and an equivalent amount of copper goes into solution as copper nitrate.

$$2AgNO_3 + Cu \rightarrow Cu(NO_3)_2 + 2Ag$$

The reverse reactions will not take place under normal conditions. The electromotive series is a very valuable aid in determining the resistance of the metals to corrosion and the stability of their compounds. In general, the more active metals are less resistant to corrosion and to the action of chemicals but their compounds are more stable than those of the less active metals.

TABLE XVI

THE ELECTROMOTIVE SERIES OF METALS

Cesium
Rubidium
Potassium
Sodium
Lithium
Barium
Strontium
Calcium
Magnesium
Aluminum
Manganese
Zinc
Chromium
Iron
Cadmium
Cobalt
Nickel
Tin
Lead
HYDROGEN
Antimony
Bismuth
Arsenic
Copper
Mercury
Silver
Palladium
Platinum
Gold
Iridium
Rhodium
Osmium

PHOTOCHEMISTRY

Radiant Energy. Photochemistry is that branch of chemistry which deals with chemical reactions produced by radiation, usually in the visible or ultra-violet regions of the spectrum. Infra-red light seems to be too inactive to produce chemical reaction, and X-rays and cosmic radiation are too penetrating to be very effective in an ordinary vessel. However, when visible or ultra-violet light strikes molecules, their outer or valence electrons may be displaced and the molecules may thus become sufficiently activated to react.

When light strikes a substance, a portion of the incident radiation is absorbed, a portion is reflected, and a portion is transmitted. Kirchhoff (1859) was the first to state clearly the relation between the emissive and absorptive powers of different bodies, namely, that **light of any given wave-length emitted by a body can also be absorbed by the same body at a lower temperature.** Expressed mathematically, this law may be written $E/A = S$, where E is the emissive power of a body, A is its absorptive power, and S is a constant. When absorption by a body is complete, $A = 1$ and $E = S$. A body which absorbs all the incident radiation and reflects none is called a **black body,** or better, a **perfect radiator.**

Kirchhoff's law offers a satisfactory explanation of the Fraunhofer lines (dark lines) in the solar spectrum, attributing them to the absorption of certain wave-lengths (i.e., those emitted at higher temperature) by the sun's gaseous atmosphere which is composed of vaporized elements from the sun's hot center. Thus the astronomer has been able to determine the composition of the sun.

In 1879, Stefan discovered an empirical relation between the total radiation of a body and its temperature. He believed this relation to hold for all bodies, but Boltzmann (1884) derived the same relation thermodynamically and showed that it is strictly applicable only to black bodies. The Stefan-Boltzmann law states that **the total radiation from a black body (perfect radiator) is directly proportional to the fourth power of the absolute temperature.** Expressed as an equation the law is,

$$S = \sigma T^4$$

where S is the total radiation, T is the absolute temperature, and σ is a constant.

In 1900, Planck advanced the idea that radiation is emitted and absorbed discontinuously in integral multiples of a fundamental unit which he called a **quantum** ϵ, and that the energy of a quantum is proportional to the frequency of the light. This relationship was found to hold true over the whole range of the spectrum and it led to the **quantum** theory, the fundamental equation of which is $\epsilon = h\nu$, where ν is the frequency of the light and h is Planck's constant 6.55×10^{-27} erg-second.

A number of interesting phenomena are accompanied by the emission of visible light, for example, luminescence (" cold-light "), chemiluminescence, fluorescence, phosphorescence, triboluminescence, and electroluminescence (cathodo- and radioluminescence).

Absorption and Reflection. We have just considered the laws governing the emission of light and now turn to a brief discussion of the laws which deal with the absorption and reflection of light. According to Lambert's law, the intensity of light, I, after passing through a uniformly absorbing medium depends on the intensity of the incident light, I_0, and the thickness, l, of the absorbing medium. It may be expressed mathematically by the following equation:

$$k = \frac{1}{l} \ln \frac{I_0}{I}$$

where k is a constant which is characteristic of the absorbing medium and the wave-length of the light. It is called the *absorption coefficient.* This equation written in the exponential form becomes

$$I = I_0 e^{-kl}$$

In 1852, Beer extended Lambert's law to the absorption of light by solutions. He pointed out that in solutions the absorption depends not only on the thickness but also on the concentration. Beer's law may be written as follows,

$$I = I_0 e^{-k'lc}$$

where c is the concentration of the solution and k' is a constant characteristic of the solute and the wave-length. Another way of stating Beer's law is: When equal heights or thicknesses of two solutions give the same intensity of color, the concentrations of the solutions are equal; when equal color intensity is obtained from different heights of two solutions, the concentrations are inversely proportional to the heights. Beer's law is the basis of colorimetric analysis and holds only where the color formations in the solutions to be compared are perfectly formed and stable, or are the same in both solutions.

Photochemical Laws. As early as 1818 Grotthuss stated that **only those rays of light which are absorbed can produce chemical change.** However, it does not follow that a chemical change must accompany the absorption of light, and, as a matter of fact, the absorbed radiation is usually converted into heat. Only a portion of the rays absorbed are directly involved in effecting a chemical change.

In the interpretation of photochemical reactions, Einstein's (1912) **law of photochemical equivalence** has proved to be of great value. This law states that **in the primary photochemical process each molecule is activated by the absorption of 1 quantum of radiation.**

The Spectroscope. The spectroscope was invented by Bunsen and Kirchhoff about 1860 and has been one of the most important research instruments during the past three-quarters of a century. One of its principal uses is in the detection of elements. The instrument (Fig. 25) is shown diagrammatically in Fig. 26. It consists essentially of a triangular prism *A*, which disperses the light rays of different wave-lengths, producing a spectrum; a tube *B* with a collimator containing an adjustable slit, which admits the light; a small telescope *C* for viewing the spectrum; and a scale *D* for determining the relative positions of the spectral lines. When a sodium-containing flame is viewed through the

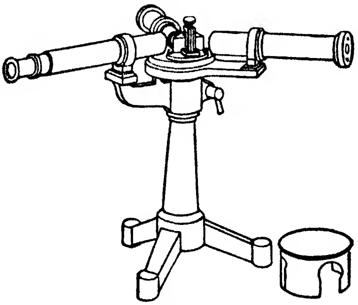

Fig. 25

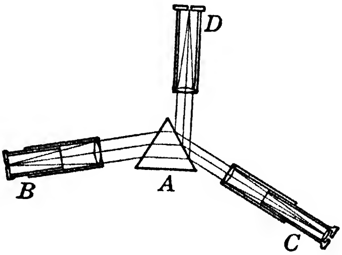

Fig. 26

telescope, a very brilliant yellow line (actually two lines close together) is observed. Potassium gives a red line and a blue line; lithium gives a red line and an orange line; thallium produces a green line; and so on, each element under appropriate conditions exhibits a characteristic spectrum. Emission spectra of a few of the more common elements are shown in the plate opposite.

The spectroscope is the most sensitive instrument known for the detection of elements. In fact, it was by means of the spectroscope that helium was discovered. It was observed in the solar spectrum during the eclipse of the sun in 1868 but was not isolated until 1895, when Ramsay liberated it from a specimen of uraninite (clevite) by heating the mineral with sulfuric acid and collecting the gas. Upon observing the spectrum of this gas, it proved to be identical with that of solar helium.

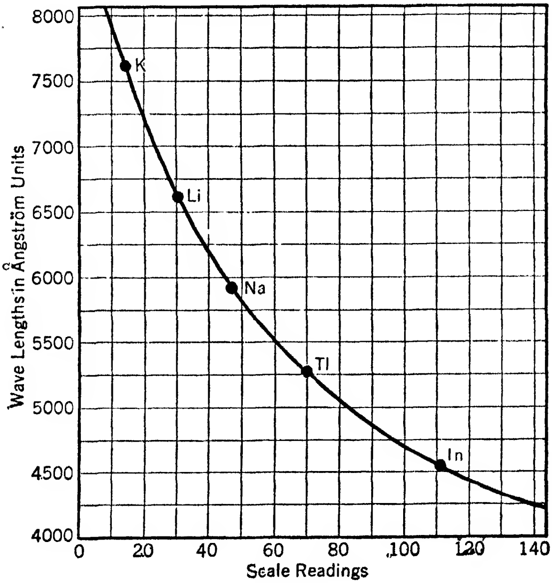

Fig. 27

Calibrating the Spectroscope. The spectroscope is first adjusted. This is accomplished as follows: Place a lighted Bunsen burner in front of the collimator about 4 inches from the slit. Introduce into the flame, near its base, a little sodium chloride held in a loop on the end of a platinum wire. Look through the telescope, rotate the slit until the sodium line is vertical, and then focus sharply by moving back and forth the sliding tubes of the telescope and collimator containing the slit. Illuminate the scale with a small electric bulb and then sharply focus the scale. The mean wave-length of the two fine sodium lines is 5893×10^{-7} mm. Since 10^{-7} mm. is an Ångström [2] unit (Å.), the mean wave-length of the sodium lines is 5893 Å. Record the scale reading corresponding to the sodium lines. In a similar manner observe a number of other elements and record the scale readings corresponding to one or more characteristic spectral lines of each. Now plot scale readings as abscissas and the corresponding wave-lengths as ordinates. Draw a smooth curve through all the points, thus making it possible to convert intermediate scale readings into wave-lengths. A typical calibration curve is shown in Fig. 27.

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[2] A Swedish physicist noted for his research in optics.

CHAPTER XXII

ELECTRICAL THEORY OF MATTER, RADIOACTIVITY, AND ATOMIC STRUCTURE

ELECTRICAL THEORY OF MATTER

According to the kinetic-molecular theory all matter, solid, liquid, and gaseous, is made up of extremely minute particles called molecules, each of which has properties identical with those of the whole mass. Furthermore, the molecules are composed of atoms of elements combined in definite numbers, and the molecules are in continuous motion. The energy of motion of the molecules is called kinetic energy. It is believed that all matter has a discontinuous structure, that is, it is made up of distinct particles. Particles of matter in the gaseous state have much greater freedom of motion than those in the liquid and solid states. Gases are practically non-conductors of electricity under ordinary conditions. However, if a sufficiently high potential difference is established between two points in a gas, an electric spark is produced between the points. If the gas be sealed in a glass tube which is connected to a vacuum pump and the pressure is gradually lowered, a marked difference in the character of the discharge and the potential necessary to produce it will be observed. As the pressure is lowered the spark becomes more uniform and broader until finally, when a pressure of a few tenths of a millimeter is reached, the cathode (negative electrode) becomes surrounded by a luminous layer and between this and the anode there appears a series of striations separated by dark spaces. The current is conducted partly by electrons and partly by gas ions. When the outer electrons are removed from molecules they become positive gas ions, and when electrons attach themselves to molecules, negative gas ions are formed. These gas ions are similar to electrolytic ions except that they are not governed by stoichiometrical valence numbers and they are formed largely by the current itself, whereas electrolytic ions are present before the current passes.

When the pressure is reduced to about a hundredth of a millimeter the luminous striations vanish and the walls of the glass tube opposite the cathode become faintly luminescent, the color depending on the kind of glass. This phenomenon, called **cathodoluminescence,** is due to the bombardment of the walls of the glass tube by negative particles projected from the cathode. These **cathode rays** are streams of electrons.

The discovery and study of the properties of cathode rays by Sir J. J. Thomson, Sir William Crookes, and others laid the foundation for our modern theory of atomic structure. We may briefly summarize a number of the properties of cathode rays: they travel in straight lines normal to the cathode; they are stopped by opaque objects and cast the shadow of such an object placed in their path; they can produce mechanical motion; they cause a rise in the temperature of objects which they strike; they cause many substances to show cathodoluminescence; they can be deflected from their rectilinear path by either a magnetic field or an electrostatic field; they can penetrate thin sheets of metal; they cause the formation of fog when directed into supercooled water vapor; and, finally, cathode rays carry a negative charge which has been found to have a value of 4.774×10^{-10} electrostatic unit. The determination of the charge on the electron permits the most accurate method for calculating Avogadro's constant, N, i.e., the number of molecules in a gram-molecule. This turns out to be 6.06×10^{23} molecules. The mass of the electron is 1/1845 times the mass of the hydrogen ion. Since hydrogen has an atomic weight of 1.0078, it follows that the electron must have an " atomic weight " of 0.00054.

Positive Rays. Electrons move with an enormous velocity under the influence of a high potential in a vacuum tube, and when they strike residual gas atoms in the tube, they remove one or more electrons, leaving the atoms with a positive charge. The anode immediately repels these positively charged atoms, sending them with high velocity towards the cathode. By using a perforated cathode, the positively charged atoms pass through the cathode and their properties may then be studied. They are called **positive rays,** and Aston has developed an apparatus, based upon Sir J. J. Thomson's method for determining the masses of positively charged particles, which he calls a "mass spectrograph." By means of this apparatus, Aston (1919) was able to obtain direct experimental evidence of **isotopes,** i.e., elements that have practically the same chemical and spectroscopic properties but differ in atomic weight. Several years before Aston's work, Soddy and others had predicted the presence of such elements. In fact, Soddy even placed different elements in the same position in the periodic table in his attempt to assign places for the radioactive elements and proposed the name isotope for elements occupying the same position in the table.

Aston discovered that many elements are mixtures of isotopes, and, by determining the relative abundance of the different isotopes present in these elements, he was able to explain why some of them have atomic weights which are not whole numbers. The results of this work have established the unitary theory of matter and, hence, have confirmed the essential correctness of the more than a century old hypothesis of Prout (see page 14).

Atomic Numbers. The subject of atomic numbers has already been discussed, and so the reader is referred to page 20. It might be mentioned that, when Moseley prepared his table of atomic numbers in 1914, there were six vacant spaces, corresponding to six missing elements. Since that time at least four of these have been discovered.

RADIOACTIVITY

In 1896, Becquerel discovered that certain fluorescent substances give off rays which affect a photographic plate, even when it is inside the holder. Further experiments proved that this action was not due to fluorescence. For example, uranous and uranic salts exert a similar photographic action, but uranous salts are not fluorescent. Moreover, Becquerel found the photographic activity of these salts to be proportional to their uranium content. Many of the properties of the rays emitted by uranium salts differ from those of X-rays, and the rate of emission is constant, irrespective of the temperature. This spontaneous radiation is a property of the element uranium, and it is called **radioactivity.**

At the suggestion of Becquerel, Madame Curie studied the radioactivity of uranium minerals and found them to be more active than the pure uranium salts. This led her to suspect that the uranium minerals contained a new element which was more radioactive than uranium. By working up more than a ton of uranium residues, Madame Curie and her husband discovered a radioactive element associated with bismuth and named it **polonium,** in honor of her native land, Poland. Later the Curies discovered another extremely active element associated with barium in the alkaline-earth group, and because of its great radioactivity, Madame Curie named it **radium.** In 1910 Madame Curie obtained metallic radium. During the past year or two Frederick Joliot and his wife, Irène Curie-Joliot, have succeeded in producing "artificial" or "induced" radioactivity, e.g., synthetic radio-sodium.

Besides the radioactive elements uranium, polonium, and radium, the elements thorium, actinium, ionium, and a number of short-lived elements are radioactive.

Radioactive substances emit three distinct types of radiation called by Rutherford the α-, β-, and γ-rays, respectively. A few of the characteristics of these rays are as follows:

α-rays correspond to the positive rays (also called "canal rays") in a vacuum tube. They consist of particles with a mass of four (i.e., He atoms), carrying two positive charges, and move with a velocity approximately one-tenth that of light. They possess very little penetrating power or photographic action, but have great ionizing power.

β-rays are negatively charged particles and are the same as cathode rays, except that they move much faster and, hence, have greater penetrating power. Their speeds vary from four- to nine-tenths that of light. The ionizing power of β-rays is much less than that of α-rays.

γ-rays are identical with X-rays but on account of their shorter wave-length and greater frequency they are more penetrating. Being electrically neutral, they cannot of course be deflected from a rectilinear path by either electric or magnetic fields.

ATOMIC STRUCTURE

The nuclear theory of the structure of the atom now rests upon good experimental evidence. We have just seen that the spontaneous disintegration of radioactive elements indicates that the nuclei of heavy atoms are made up of helium atoms and electrons. When α-particles are shot into a chamber filled with supersaturated water vapor, they travel in straight lines as can be plainly seen by their "fog-tracks." Occasionally a branched track is seen, and this is believed to be due to a direct hit on the nucleus of an atom. This indicates that the mass of an atom is concentrated in a nucleus which occupies only a small fraction of the total volume of the atom. By means of the mass spectrograph it has been possible to measure the mass of the nucleus, and the determination of the atomic number by X-ray analysis shows the number of excess positive charges on the nucleus. There is only one unit of negative electricity—the **electron.** Positive electricity is usually associated with a hydrogen nucleus to form the **proton** (or H^+ ion). Recently a fundamental unit of positive electricity, the **positron,** has been discovered by Anderson. According to the modern atomic theory, the atom contains a compact nucleus composed of protons cemented together by electrons and surrounded by outer electrons which exactly equal in number the total excess positive charges on the nucleus. The mass of an atom is equal to the total number of protons in the nucleus and these are grouped as far as possible into secondary units, i.e., helium nuclei, each of which contains four protons and two electrons. It is obvious that the more than a century old hypothesis of Prout (1815) is probably essentially correct. According to Prout's hypothesis, all the elements are built up of hydrogen.

The difference between the total number of protons and total number of electrons in the nucleus is equal to the atomic number. Also, it has been shown that the fractional atomic weights of certain elements are due to the fact they are mixtures of isotopes.

As stated above, the number of electrons outside the nucleus of a neutral atom is exactly equal to the number of positive charges on the nucleus, that is, the atomic number. According to the modern theory, these **planetary electrons** are arranged in definite, stable shells, or groups, around the nucleus, and only the outermost electrons are involved in the valence, the position in the periodic table, and the chemical properties of the element. In 1916, G. N. Lewis proposed a cubic atom in which the planetary electrons are arranged at the eight corners. The cubic or static atom was elaborated upon by Langmuir in 1919. This simple atomic model has proved very helpful to the chemist in studying chemical properties, but a much more complicated model is required to represent the facts obtained in spectroscopy.

The Elements and the Electron Theory. Of the ninety definitely known elements, seventy are metals and twenty non-metals.

The **electron theory** of the structure of the atom helps us to distinguish between a metal and a non-metal. According to this theory all the elements are made up of but two kinds of particles: **electrons** and **protons.** The electron is a unit charge of negative electricity and is about 1845 times lighter than the hydrogen atom. The proton is a unit charge of positive electricity and is about 1845 times heavier than the electron but 1845 times smaller. All matter is now believed to be made up of these electrical particles. All atoms are electrically neutral, and hence each atom contains an equal number of electrons and protons. The different elements differ only in the number and arrangement of their electrons and protons. In other words, all matter is composed of electricity.

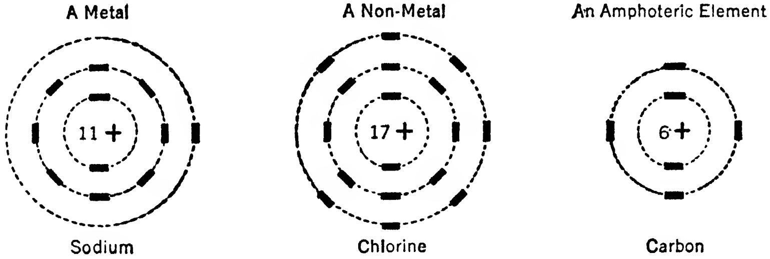

FIG. 28

(*a*) One electron in outside ring.
(*b*) Lender of one electron.
(*c*) Valence +1.

(*a*) Seven electrons in outside ring.
(*b*) Borrower of one electron.
(*c*) Valence −1.

(*a*) Four electrons in outside ring.
(*b*) Lender or borrower of four electrons.
(*c*) Valence ±4.

According to the electron theory, each atom is a miniature solar system, with one or more protons as a nucleus, and at a relatively great distance from it revolve **planetary electrons.** The number of planetary electrons in an atom of an element is called the atomic number (Moseley number) of that element. Thus hydrogen, the element with the lowest atomic weight, has one electron outside the nucleus and its atomic number is, therefore, 1. Uranium, the element with the highest atomic weight, has 92 electrons outside the nucleus, and hence its atomic number is 92.

We may now define the **valence of an element as the number of electrons which its atom must borrow or lend to complete its outermost ring.** A metal is a **lender of electrons,** as the outermost ring of its atom contains less than half to complete it. A non-metal is a **borrower of electrons,** as the outermost ring of its atom contains more than half of the number of electrons required to complete it. An amphoteric element is one whose atom has its outermost ring half completed or nearly half completed. Such atoms may either borrow or lend electrons. Carbon is a common example of an amphoteric element.

The metals have many properties in common, both physical and chemical. The more common physical properties of metals are: they exhibit a definite shine or luster, are malleable, are ductile, are good conductors of heat and electricity, and, with the exception of mercury, all are solids at room temperature. All metals are crystal-like. They range in specific gravity from 0.53 for lithium to 22.5 for osmium. In hardness, the metals range from those as soft as wax, for example the alkali metals, to those that are very hard, as, for example, tungsten. The metals combine with oxygen to form oxides which are basic anhydrides, for example, calcium oxide, CaO, and magnesium oxide, MgO. The metals interact with acids, liberating hydrogen or some other gas. They combine with the non-metals to form salts. Some of the metals, the amphoteric ones (aluminum, zinc, etc.), react with bases to form salts and hydrogen gas.

CHAPTER XXIII

COLLOIDS

If we add water to sugar or to table salt, each will dissolve to form a solution. These solutions will pass completely through a filter paper. They appear water-clear and homogeneous in the light, but when a beam of light is passed through them in a darkened room they remain perfectly dark. The explanation of this is that the individual particles of the solute, i.e., the sugar or salt, have become intimately mixed with the solvent. We say that the component substances of the solution have become molecularly dispersed in each other. On the other hand, if we shake up some sand with water we find that the particles of sand remain suspended for a short time but soon completely settle to the bottom of the vessel. Here we have an ordinary dispersion or suspension. Now, matter may also assume a state of subdivision intermediate between true solution (molecular or ionic subdivision) and ordinary dispersion or suspension, as in the suspended particles of sand. In this state of subdivision matter is said to be **colloidal,** and if the particles are mixed with a substance (in which they do not dissolve to form a "true" solution and do not agglomerate) the resulting mixture is called a **colloidal solution.** It would be better to call the mixture a colloidal suspension. The particles are really in suspension, although they are too small to be seen with the naked eye, or even when magnified 2000 times with a good microscope of the ordinary type. In fact, the particles are so small that the "solution" may appear perfectly clear and they will pass through an ordinary paper filter. However, if a strong beam of light is passed through the colloidal solution (suspension) in a darkened room, the presence of the highly dispersed particles is revealed, the visibility of the beam being due to the scattering effect of the minute particles. The particles are aggregates of molecules. This scattering effect was first observed by Tyndall and is known in his honor as the **Tyndall phenomenon.** Everyone is familiar with the beam obtained when the sun shines through a hole in the shade into a darkened room. And if the room has just been swept, or if it contains smoke, the beam is intensely bright. The dust or smoke particles serve as thousands of little mirrors, and the larger ones may be seen as tiny bright spots. Similarly, the minute particles in a colloidal solution serve as "mirrors" to reflect the light.

The importance of colloid chemistry, both from a theoretical and from a practical standpoint, may be seen from the wide field which it covers. To illustrate, the following list of applications has been compiled chiefly from Bancroft.[1] A knowledge of colloid chemistry is necessary in order to understand the following: living matter, blood serum, and the sap of plants; cement, bricks, pottery, porcelain, glass, enamels; oils, greases, soaps, candles; glue, starch, and adhesives; paints, varnishes, lacquers; rubber, guttapercha, celluloid, and other plastics; hides, leather, paper; textiles; filaments, casts, pencils, and crayons; inks; roads, foundry cores, cokes, asphalt; graphites; zinc, phosphorus, sodium, and aluminum; contact sulfuric acid; hardened oils; beer, ale, and wine; milk, cream, butter, cheese, and casein products; the principal articles of food; cooking; washing; dyeing; printing; ore flotation; water purification; sewage disposal; smoke prevention; photography; wireless telegraphy; illuminants; comets; pharmacy; physiology. In short, says Bancroft, "colloid chemistry is the chemistry of everyday life."

The first systematic study of colloids was made by Thomas Graham (1861) an English chemist. The name "colloid," derived from the Greek word κολλα meaning glue, is also due to Graham because of his observation that colloid substances are usually gelatinous or non-crystalline, like glue. Wilhelm Ostwald has included some of Graham's articles in his collection of "Klassiker der exakten Wissenschaften."

We may summarize Graham's work under two heads: (1) diffusion experiments, and (2) the preparation of "colloidal" solutions.

Graham's Diffusion Experiments. Graham observed that some substances when dissolved passed freely through organic membranes into the pure solvent surrounding the membrane, whereas many others either did not diffuse, or diffused extremely

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[1] Bancroft, "Applied Colloid Chemistry," p. 2, third edition, McGraw-Hill Book Co., New York, 1932.

slowly. He used animal membranes and parchment paper in these experiments, and called the process "dialysis." He also noted that those substances which diffused rapidly were, in general, crystalline, e.g., salt, sugar, potassium nitrate, potassium sulfate, magnesium sulfate, etc. On the other hand, those substances that failed to pass through the membranes, or diffused very slowly, usually occurred in a non-crystalline or even gelatinous form, e.g., silicic acid, starch, gelatin, gums, glue, etc. Accordingly, he divided chemical substances into two classes: (1) crystalloids and (2) colloids. He believed that the distinction between a crystalloid and a colloid was fundamental and suggested that it was due to some molecular condition. He devised a "dialyzer" (Fig. 29) which he used to separate crystalloids from colloids.

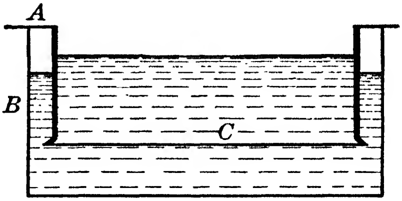

FIG. 29.—*A*, tambourine-like frame; *B*, vessel of water; *C*, parchment paper.

Graham's Preparation of Colloidal Solutions. In the course of his experiments, Graham discovered that many substances generally known to be insoluble could, by certain special methods, be made to go into solution, or at least what appeared to be solution. He prepared and carefully investigated a number of such solutions, e.g., those of silicic acid, tungstic acid, aluminum hydroxide, chromium hydroxide, ferric hydroxide, etc. Most of these appeared to the naked eye just like any ordinary solution, that is, they were perfectly clear and apparently homogeneous. However, they did not diffuse through parchment or animal membranes, and on this account Graham called them "colloidal solutions," or "sols." The term "sol" is still in use. Another striking thing about the behavior of these sols was the fact that very small amounts of electrolytes, which did not react at all with the dissolved substances, caused radical changes in their condition. For example, the addition of a small amount of any neutral salt caused the aluminum hydroxide, chromium hydroxide, and ferric hydroxide to precipitate or coagulate in the form of flocculent masses. A trace of carbon dioxide would cause the silicic acid sol to set to a translucent jelly. Graham called these transformation products of sols "gels," a term which is still used.

Some Early Work on Colloids. Although Graham was the first to carry out a systematic study of colloids he was by no means the first to observe what would now be termed sols. Moreover, his distinction between colloids and crystalloids is no longer held. However, modern colloid chemistry began with Graham (1861), and he rightly may be called the "father of colloid chemistry."

Berzelius between 1808 and 1833 prepared and made observations on a number of substances in colloidal solution. For example, he made what we now call sols of sulfur, arsenious sulfide, silicic acid, tellurium, etc. That he correctly interpreted his "solutions" as really being very finely divided particles suspended in a liquid may be seen from the description of arsenious sulfide sol which he gives in his "Lehrbuch" (1844).[2]

In 1810 Gay-Lussac made the first observations on the hydrolysis of a salt resulting in the formation of colloidal solution. He hydrolyzed aluminum acetate and obtained a sol of aluminum hydroxide. Later, Berzelius (1833) described the preparation of β-silicic acid by the hydrolysis of silicon sulfide.

In 1853 Crum obtained pure aluminum hydroxide sol by hydrolysis of aluminum acetate but failed to get ferric hydroxide sol from ferric acetate. Péan de Saint Gilles, however, succeeded in getting the ferric hydroxide sol the following year. Both these investigators carried out precipitation reactions with neutral salts.

Wackenroder in 1846 discovered that a colloidal solution of sulfur is obtained by the action between sulfur dioxide and water, and in 1850 Sobrero and Selmi made a careful study of the sol. After describing how the sulfur is coagulated by the addition of salt and how it may be brought back into suspension by repeated washing which removes the salt, they go on to say:

> This enormous quantity of sulfur is, one would be inclined to say, dissolved, for it hardly affects the limpidity of the liquid. . . . Sulfur can thus be modified in an extraordinary manner by the substances present at the time of deposition, these adhering obstinately, probably by simple adhesion, and can either acquire the property of emulsifying in water, or assume a state of aggregation which prevents it dividing up in water. It thus appears that sulfur exhibits phenomena analogous to those observed with many other substances, which possess the power of dispersing and divid-

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[2] Cf. W. W. Taylor, "The Chemistry of Colloids," p. 12, second edition, Longmans, Green & Co., New York, 1923.

ing themselves in a liquid, without completely dissolving in it, as, e.g., soap, starch, and prussian blue, on which one of us (Selmi) has previously made observations similar to those now described. These facts are related to a set of phenomena which M. Selmi has classed together under the name of pseudo-solutions. The number of pseudo-soluble substances seems to be pretty large.[3]

The history of colloidal solutions of the metals dates back to the alchemists. Some of these metal sols were used in the early days as medicines—for example, the red and purple liquids obtained by the reduction of gold chloride and called by the alchemists "aurum potabile." Methods of making these liquids are given in Marcquer's "Dictionnaire de chemie" as late as 1774. The diary of one John Evelyn, an Englishman, records under date of June 27, 1653, reference to a small phial of aurum potabile which was sent to him and the wonderful cures the liquid was reported to have made in Paris.

The metal sols formed by cathode reduction were generally thought to be hydrides. However, Ruhland in 1815 and Poggendorf in 1848 said that they were suspensions of the metals in a very fine state of division.

Wöhler, in 1839, working with silver citrate, found that when heating it in a current of hydrogen a residue was left which dissolved in water to give a red solution. He called the substance a sub-salt of silver. A half century later Muthmann (1887) prepared some of the red liquid and showed that, upon dialyzing, not only did the red substance fail to diffuse through the membrane, but also that only undecomposed silver citrate was found in the outside water. This experiment is the first one on record where dialysis is applied to a metal sol. Various methods of reducing silver to yield concentrated sols were developed by Carey Lea (1889). He called the coagulum from these sols "allotropic silver."

In 1857, four years before Graham published his first paper on colloids, Faraday made some fundamental observations on gold sols. He prepared violet and purple liquids by reducing very dilute solutions of gold chloride with phosphorus dissolved in ether. He said that the color of the liquids was due to metallic gold in a very finely divided state. Moreover, he noted the effect small amounts of electrolytes had on the stability of the liquids. The glass vessels

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[3] *Ann. de chim. et de phys.* (iii) **28**, 210 (1850); Taylor, *op. cit.*, p. 13.

in which he kept the liquids were also observed to have influence on the stability of the sols. Faraday found that "a little jelly" increased the stability of the liquids. Such substances we now know under the name of "protective colloids." Many of them have been found and are now in every-day use as "stabilizers" or "protectors" for colloidal preparations. It is interesting to know that some of Faraday's gold sols are now in the Royal Institution, England, and that one or two of them still show a faint pink tinge. The others have coagulated.

Up to 1890 much time had been given to the preparation of sols, but the twenty years following saw great strides made in the more fundamental aspects of the subject. Linder and Picton (1892) and Hardy (1900) made important studies on the effects of electrolytes. The invention of the ultramicroscope by Zsigmondy and Siedentopf in 1903 marked a new era in colloid chemistry. Research was greatly stimulated by its invention. In 1909 and 1910 the first comprehensive works on colloid chemistry were published by R. Zsigmondy, by Wo. Ostwald, and by H. Freundlich. In these books the great mass of uncoordinated material which had accumulated was collected and treated thoroughly and systematically.

The outstanding advance in colloid chemistry since Graham's work (1861–1864) has been the proof that there are no "colloids" in the sense in which Graham defined them. That is to say, there is no distinct class of substances having peculiar properties designated by the term but **any substance can,** under appropriate conditions, appear as a **colloid.** The term **colloid,** therefore, refers to a **state** of matter and not to a **kind** of matter. A colloidal substance may or may not be amorphous. Colloidal gold has been definitely proved to be crystalline at times and is probably always crystalline. Sodium chloride is a well-defined crystalline substance, and yet we can prepare colloidal solutions of it in organic liquids by several methods. Therefore, "we now speak of a **colloidal state** instead of a **colloidal substance,** and we call any phase colloidal when it is sufficiently finely divided or dispersed (Wolfgang Ostwald, 1909), without committing ourselves definitely as to what degree of subdivision is necessary in any particular case." [4] Von Weimarn was the first to state the conditions necessary for obtaining any given substance in colloidal solution. He prepared sols of more than four hundred substances. Nearly all the metals and many of the

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[4] Bancroft, *op. cit.*, p. 1.

non-metallic elements have been obtained in the colloidal state. Svedberg has even succeeded in getting the alkali metals in the colloid state by employing a special kind of apparatus and using organic liquids at low temperatures. A large number of hydroxide and sulfide sols have also been prepared. All these sols of inorganic substances have two fundamental characteristics in common: (1) they do not diffuse through membranes, and (2) they undergo marked and, for the most part, irreversible changes upon the addition of electrolytes (usually in very small amounts). Upon the addition of electrolytes, either the "dissolved" substance is coagulated or the whole liquid sets to a jelly.

The inorganic sols are prepared by well-defined methods. In contrast to these artificially prepared colloidal solutions is a large group of substances which dissolve at once to form colloidal solutions. In fact, true solutions of them are not known and they do not occur in the crystalline state. To this group belong the materials from which all living organisms are built, e.g., the proteins, cellulose, starch, and many other carbohydrates. Here, also, belong many dyes, rubber, cellulose, esters, glue, etc.

Disperse Systems. Another great advance since Graham's time, "of equal importance is the demonstration that the colloidal state is only a special case of the *disperse system,* a concept and term first introduced by Wolfgang Ostwald." By a disperse system is meant " a system of two phases differing in one or more physical properties, and having *a large surface of contact, or interface.* To obtain a surface large in proportion to the volume of to least one phase, it is necessary to reduce one or more linear dimensions of the latter: if one is so reduced we have films; if two, filaments; and if all three are small, particles bounded by a closed surface, e.g., spherical, of one phase distributed in the other. All three configurations occur in nature in many variations. . . ." [5] Suppose that we consider the third kind, i.e., where all three dimensions of one phase are small. In such a system we can pass in one phase from one part to another without coming in contact with the second phase, namely, the finely divided phase. Hence, we speak of the former as the **continuous phase** or **dispersion medium** and the latter as the **dispersed phase.** Many synonymous terms for these two phases occur in colloid literature, e.g., synonymous

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[5] Hatschek, "An Introduction to the Physics and Chemistry of Colloids," p. 7, fifth edition, P. Blakiston's Son & Co., Philadelphia, 1926.

with **dispersion medium** we find: **closed phase, enveloping phase, external phase, dispersing phase**; and synonymous with **dispersed phase: discontinuous phase, subdivided phase, internal phase, disperse phase.** Examples of some commonly known disperse systems will serve to illustrate what is meant by the dispersed phase, and the dispersing phase or dispersion medium.

> In fog the rain drops are the dispersed phase and the air the dispersing phase, while the solid particles are the internal phase in the case of smoke. When a milky liquid is obtained by precipitating barium sulfate in the cold, the barium sulfate is the dispersed phase and the solution the dispersing phase. In emulsions of oil in water, the oil is the internal phase because it is present in drops. When benzene is emulsified to a solid jelly in a small amount of soap and water, we have a mobile liquid dispersed in a viscous mass. Bread or Ivory soap might be considered as a system with air as internal phase, and a fairly solid external phase. . . . True ruby glass consists of gold as dispersed phase in glass as a non-crystalline dispersing phase. With salt colored by exposure to cathode rays, we have metallic sodium as internal phase in an external phase of crystalline sodium chloride.[6]

Bancroft says that if we adopt "the very flexible definition that a phase is called colloidal when it is sufficiently finely divided, colloid chemistry is the chemistry of bubbles, drops, grains, filaments, and films, because in each of these cases at least one dimension of the phase is very small. This is not a truly scientific classification because a bubble has a film around it and a film may be considered as made up of coalescing drops or grains." This classification, however, is a convenient one for many purposes.

It will be observed that in a colloidal solution we are dealing with a system of two phases, in other words, the "solution" is **heterogeneous** and not **homogeneous** as in true solutions (one phase systems). The dispersed phase and the dispersion medium differ from one another in one or more physical properties. However, we must not forget that the two phases may have one such property in common. For example, glass dispersed in cedar oil of the same index of refraction is optically homogeneous in all other properties. On the other hand, particles suspended in a liquid having the same density will be homogeneous as far as the effects of the force of gravity go, but will be optically heterogeneous. A

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[6] Bancroft, *op. cit.*, p. 1.

single physical property, therefore, must never be taken to settle the question as to whether or not a "solution" is colloidal.

There are various ways of classifying disperse systems, in fact, any one of a number of physical properties might serve as a basis of classification. Wo. Ostwald has classified disperse systems based upon the **state of aggregation** of the phase, that is, whether solid, liquid, or gaseous. Such a classification gives us nine possible types, since both phases may be in the same state of aggregation. One of the nine, that in which both phases are gaseous, is strictly limited, "since gases are miscible in all proportions and we cannot have particles of the disperse phase larger than molecules." The remaining eight types are given in the following table.

TABLE XVII

Dispersion Medium	Disperse Phase	Examples
1. Solid	Solid	Blue rock salt (sodium dispersed in colloid state), ruby glass, many colored minerals
2. Solid	Liquid	Minerals with enclosed liquid
3. Solid	Gas	Minerals with enclosed gas
4. Liquid	Solid	Suspensions
5. Liquid	Liquid	Emulsions
6. Liquid	Gas	Froth, foam
7. Gas	Solid	Smoke, cosmic dust
8. Gas	Liquid	Fog, mist

According to Ostwald, all disperse systems may be grouped according to the size of the particles of the disperse phase.

DISPERSE SYSTEMS

Coarse Dispersions	Colloids	Molecular Dispersoids
	Increase in degree of dispersion →	
	0.1 μ to 1.0 mμ	
Diameters greater than 0.1 μ do not pass through paper filters; microscopically analyzable.	Pass through paper filters; cannot be analyzed microscopically; do not diffuse or dialyze.	Diameters smaller than 1.0 mμ pass through paper filters; cannot be analyzed microscopically; diffuse and dialyze.

Perrin and also Freundlich classify colloids according to their behavior towards electrolytes, or otherwise stated, on the degree of affinity between the two phases. Those that are greatly influenced (e.g., coagulated) by the addition of small quantities of electrolytes are called **lyophobe** (little affinity between the phases); those upon which electrolytes have little effect are termed **lyophile** (marked affinity between the phases). Although differences in behavior towards electrolytes constitute an important distinction it does not go directly to the root of the matter as does Ostwald's classification. The terms **lyophobe** and **lyophile** are approximately equivalent to **suspensoid** and **emulsoid**, respectively. In emulsoids, both the dispersed phase and the dispersion means are liquid, whereas suspensoids are systems in which the dispersed phase is solid and the dispersion means liquid.

The Size of Dispersed Particles. The size of dispersed particles varies within fairly wide limits. The diameters of the particles are usually expressed in **microns,** μ (0.001 mm.) or in **millimicrons,** $m\mu$ (0.000001 mm.). Particles having a diameter greater than 1μ (coarse suspension) may be filtered out by means of an ordinary paper filter; particles dispersed in water (hydrosols) and having diameters less than 20 $m\mu$ do not settle at all, i.e., the "solution" remains clear.

The upper limit of direct measurement is fixed by the limit of visibility of the best microscope. This has been estimated by Bredig as 0.14 μ (limit of visibility at a magnification of 2250 diameters). With this magnification Bredig was not able to see the individual particles in gold sols. The lower limit is fixed by molecular dimensions. The estimated diameters of some common molecules are as follows: hydrogen 0.67 to 0.16 $m\mu$, water vapor 0.113 $m\mu$, carbon dioxide 0.285 $m\mu$, sodium chloride 0.26 $m\mu$, sugar 0.7 $m\mu$, starch 5 $m\mu$. With the ultramicroscope, particles a little less than 10 $m\mu$ in diameter may be distinguished optically. However, neither the form nor the size, nor even the color, of the particles can be determined directly by means of the ultramicroscope, since what is observed is a disc of light surrounding each particle. In the ultramicroscope a converging beam of intense light in a darkened room is passed horizontally through the liquid under examination and brought to a focus within the liquid. The spot where the beam is in focus is viewed from above through an ordinary microscope.

The Siedentopf and Zsigmondy[7] method of determining the size of colloidal particles is as follows:

Chemical analysis of the sol gives the mass m of the disperse phase in unit volume of the sol; the number of particles n in unit volume of the sol is obtained by a direct count of the number of particles in the illuminated volume of the sol in the ultra-microscope. This volume is fixed by the depth of the illuminating beam, and by the area of the field (micrometer squares) in which the particles are counted. The volume v of the particle is given by:

$$v = \frac{m}{nd}$$

d being the density of the particle (the density of the substance in ordinary masses is taken). The linear dimension is calculated from the volume, on the assumption that the particle is a cube or a sphere. The dispersity of a sol is usually expressed in terms of the diameter.[8]

It is better, however, to use the **specific surface** to express the degree of dispersion. The specific surface is the surface divided by the volume. For a cube having a side l in length, the surface is $6l^2$, the volume l^3, and the specific surface is, therefore, $6/l$. From this it follows that a 6-cm. cube has unit specific surface.

It may be noted here that the surface energy of a substance is negligibly small unless its specific surface is 10,000. Surface energy is equal to the surface tension (an " intensity " factor) multiplied by the surface (a " capacity " factor). Compare the volume energy of the gas state which is equal to pressure (" Intensity " factor) × Volume (" Capacity " factor). Owing to the small numerical value of the " intensity " factor, surface energy forms an insignificant fraction of the total energy of a liquid or solid, unless the development of the surface is extraordinarily great.

The ultramicroscopic method for the determination of the size of colloidal particles is very uncertain. Often the chemical composition of the highly dispersed particles is unknown or uncertain. In a metal sol some of the metal may be in the form of an oxide, and may even be in solution, or it may be hydrated. Any of these factors would make the calculation incorrect.

[7] "Zur Erkenntnis d. Kolloide," p. 93.

[8] Taylor, *op. cit.*, p. 53.

In addition to the ultramicroscopic method of Siedentopf and Zsigmondy, various other methods have been used to measure the size of particles in a solution. A résumé[9] of these methods is briefly given as follows:

1. Method of measuring the density of distribution at different heights. (Perrin.) Very exact.
2. Method of the Brownian movement. (Einstein.) The accuracy is low.
3. Method of rate of settling. An application of Stokes' formula for the velocity of fall of a small sphere in a liquid. Applicable only to relatively large particles. The viscosity and density of the dispersion medium and the density of the particles must be known.
4. Method of diffusion. (Sutherland, Einstein, Smoluchowski.) Very low and applicable only to highly dispersed sols.
5. Method of absorption of light. (Garnett, Mie, Wood, Svedberg.) This method is very promising but so far it is used only to determine changes in size of the particles.
6. Method of intensity of scattered light. (Rayleigh.) This method is very sensitive and gives accurate results even with very fine suspensions.

Ultra-Filtration. If a sol is poured onto an ordinary paper filter it passes through unchanged or only slightly changed. The filter may absorb or adsorb a little at first, but aside from this there is no further loss. Emulsoids also pass through ordinary filter paper but often very slowly on account of their great viscosity.

Linder and Picton[10] filtered arsenious sulfide sols through porous earthenware and found that the size of particles varied in different samples. Barus[11] determined the size of particles in a silver sol by filtering through porous plates of graded porosity. Martin[12] used gels as filtering media and employed high pressure (30 atmospheres or more). About ten years later (1906–1908), Bechhold developed the method into a fairly simple procedure and with the added advantage that only moderate pressure is needed (seldom more than 5 atmospheres). He called the process " ultrafiltration " in allusion to the ultramicroscope. Membranes similar

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[9] Henri, *Koll. Z.*, **12**, 246 (1913); *Trans. Faraday Soc.*, **9**, 47 (1913).

[10] *J. Chem. Soc.*, **61**, 148 (1892).

[11] *Sill. J.*, **48**, 51 (1895).

[12] *J. Physiol.*, **20**, 364 (1896).

to those used in dialysis are employed, but the outside is not submerged in the dispersion medium. Bechhold made a graded series of filters by impregnating filter paper, fabric, or wire gauze with gelatinous colloids of varying concentration. The filter paper, wire gauze, etc., served as support for the colloids and permitted filtration under pressure. Mixtures of collodion and acetic acid or of gelatin and water are the most suitable substances for the filters. Those of collodion are dipped into water to make them porous. The gelatin filters are allowed to stand in cold formaldehyde for several days; this treatment hardens them. The filters are then standardized. Several methods are employed to determine the size of the pores of the filters, e.g., by measuring the pressure required to force air through a membrane saturated with water, by measuring the volume of water forced through unit area in unit time by a known pressure, etc. In fact, filters having approximately known pore size may now be made by using a collodion solution of the proper concentration (previously determined by Bechhold). These filters may be used to separate the disperse phase from the dispersion medium or to concentrate emulsoids. They may also be employed to purify sols, the process being similar to purification by dialysis. Still another important application of ultra-filtration is the preparation of graded series of sols, each sol having particles of approximately the same size. Obviously the **approximate** size of particles in sols can be determined by filtering through graded series of filters and seeing which filter will just allow the particles to pass through.

The process of ultra-filtration is very complex. In addition to ordinary filtration, adsorption and dialysis may also take place.

Résumé of the Properties of Colloids. The principal characteristics of colloids are as follows:

1. **The freezing-points and boiling-points of colloidal solutions differ but little, if any, from those of the pure dispersion means (e.g., water).** The physical properties of true solutions, however, are greatly influenced by the solute. For example, the freezing-point of a solvent is lowered and its boiling-point is raised by the presence of a dissolved substance.

2. **Colloids diffuse slowly or not at all.** Graham was the first to observe that colloids have a much lower rate of diffusion than crystalloids. Diffusion is closely connected with dialysis.

Crystalloids pass through parchment paper and animal membranes readily, whereas colloids have but little tendency to diffuse or pass through.

3. **Colloidal solutions show the Tyndall phenomenon** (provided, of course, that the index of refraction of the dispersed phase is different from that of the dispersion medium—which usually it is). **If the Tyndall light-cone is viewed through a suitable analyzer, it is found to be polarized. This is the important distinction from true fluorescence.** Under similar conditions of illumination, quinine sulfate solution gives a beautiful blue cone. Certain petroleums also show light-cones, but these cones, as well as that of quinine sulfate solution, are not polarized. True solutions (molecularly dispersed solutions) do not show definite Tyndall cones. This optical difference is one of the best ways to differentiate a true solution from a colloidal solution.

4. **Colloidal solutions show the Brownian movement.**

5. **Opalescence or the "color of the colorless colloids." Opalescence varies greatly with the degree of dispersion.** Colloid systems are intensely opalescent; coarsely dispersed systems, only slightly so. True solutions (molecular and ionic dispersoids) usually show no opalescence, or if they do, the intensity is less than that of colloid systems. Note that this is the first illustration we have had where the intensity of a property of dispersed systems shows a **maximum.** This maximum occurs in the colloid realm.

6. **Intensity of color.** The coloration intensity of a substance in different degrees of dispersion **attains a maximum in the region of colloid dispersion.**

7. **Beauty and variety of colloid colors.** Not only the intensity but also the beauty and variety of colors among the colloids are noticeable. The different colors of the same metal in a colloid state are due chiefly to differences in degree of dispersion. The order of color change seems to be definite. Generally, the most highly dispersed colloid metals are yellow or orange, i.e., they absorb violet and blue light. As the degree of dispersion decreases, the color changes from yellow to orange, then red, violet, blue, and finally green.

8. **Optical rotation.** The principle of continuity of dispersed systems is also illustrated by their optical rotation. For example, tannin in water is in colloidal solution, yet some of it will pass through parchment paper and is therefore in a higher degree of

dispersion. By using membranes of different pore size, tannin sols of different degrees of dispersion can be obtained. On the other hand, tannin dissolves in organic solvents to form a true solution (molecular dispersion). If we compare the optical rotations of different tannin solutions, the coarsest tannin is seen to produce the greatest rotation; the molecularly dispersed tannin the least.

9. In addition to the properties listed above, we may add a number of others which also show the importance of the degree of dispersion upon the physicochemical behavior of dispersed systems. Take for examples such fundamental "constants" as the **maximum solubility,** the **freezing-point,** and the **melting-point** of a substance. In each instance there is a marked variation with differences in the state of division of the particles of the material concerned. As far as known, the solubility of solids (molecularly dispersed) always **increases with decrease in the size of the particles,** when the particles are very small. The old experiments of Stas showed that very finely divided silver chloride is many times more soluble than the coarse particles. Hulett determined the solubility of gypsum and found that a saturated solution at 25° C. contained 2.080 g. of $CaSO_4$ per liter, whereas when very finely divided gypsum was added to this solution its $CaSO_4$ content increased to 2.542 g. per liter. He also found mercury oxide finely ground and triturated to be more than three times as soluble as coarser pieces.

The freezing-point of water is not only lowered by molecularly dissolved substances but also by being allowed to freeze in a **dispersed** form, as for example when frozen in capillary spaces. Water soaked in a clay ball was found to freeze at $-0.7°$ C. Wet filter paper stiffens at $-0.1°$ C.

The reaction velocity of solids with liquids is proportional to the area of contact. Substances in the colloidal state present enormous surfaces and hence often show catalytic effects. Coarsely dispersed and molecularly dispersed metals have little or no catalytic action, but in the colloidal state of division they are energetic catalysts. Here, again, we find a maximum in the colloid region.

Why Colloid Particles Remain in Suspension. We have just considered a number of the characteristics shown by matter in the colloidal state. We may now ask the question: why do colloidal particles remain in suspension? Why do they not settle under the influence of gravity like ordinary suspensions? In answer to this, we may cite at least three reasons.

1. **The colloidal particles in suspension carry electrical charges, either positive or negative.** For example, the particles in an arsenious sulfide sol are all negatively charged; those in aluminum hydroxide sol are positively charged. Now, since like charges **repel** each other the electrified particles do not agglomerate to form coarse aggregates which would settle. That the colloid particles do carry electric charges is proved by the fact that they migrate to one electrode or the other when a current of electricity is passed through the suspension; i.e., the arsenious sulfide particles (negatively charged) travel to the anode, while the aluminum hydroxide particles go to the cathode. This phenomenon, known as **cataphoresis,** will be discussed subsequently. Upon reaching the electrode the charges on the particles are neutralized and agglomeration takes place.

2. **The Brownian Movement.** The colloid particles are bombarded on all sides by the molecules of the liquid in which they are suspended and hence are kept in a state of perpetual motion. If a drop of the suspension be viewed through the ultramicroscope the particles are seen as tiny bright spots in continuous movement. The particles are too small to be visible, even with the highest magnification, but they diffract the light and appear as little illuminated discs on a dark background.

3. **Protecting Films.** As early as 1857 it was observed by Faraday that the addition of a small amount of "jelly" (probably gelatin) prevented the coagulation and precipitation of metal sols. Such organic substances as gum arabic, gelatin, and the proteins are themselves largely colloidal in solution and hence they have been termed "protective colloids." It is held that they form a film around the suspended particles in a sol and thus protect them from the action of substances that ordinarily would cause coagulation. For example, arsenious sulfide sol containing a little gelatin is not coagulated by the addition of electrolytes in amounts much greater than would cause precipitation if no protective colloid were present. The protective power of these colloids varies greatly and is measured in terms of the "gold number," a term due to Zsigmondy. The gold number is the maximum number of milligrams of protective colloid that may be added to 10 cc. of a standard

gold sol without preventing a change of color from deep red to violet shades by 1 cc. of a 10 per cent sodium chloride solution.

4. The Solution Theory of Colloid Stability.

The origin of the solution forces and the reason for the electrical migration of colloidal dispersions of apparently insoluble substances such as ferric oxide, antimony sulfide, gold, etc., have gradually become apparent through years of research. It is now definitely known that these insoluble substances do not exist as such in colloidal solution. The particles in colloidal ferric oxide solution consist of a complex of Fe_2O_3 and a soluble iron salt such as $FeCl_3$; antimony sulfide hydrosol consists of a combination between Sb_2S_3 and H_2S. Formulas may be roughly written for them (ignoring the hydration water) as follows: $x\mathrm{Fe_2O_3} \cdot y\mathrm{FeCl_3}$; $x\mathrm{Sb_2S_3} \cdot y\mathrm{H_2S}$ where x and y are variable and x is always greater than y.[13] When an electric current is passed through these solutions, a brown precipitate of Fe_2O_3 settles out at the cathode and chlorine is evolved at the anode in the iron oxide hydrosol, while in the antimony sulfide sol, a red deposit of Sb_2S_3 is deposited at the anode and hydrogen gas is liberated at the cathode. This shows that the migrating ions are:

$$\begin{array}{cc} \dfrac{x\mathrm{Fe_2O_3} \cdot y\mathrm{Fe^{+++}}}{2y\mathrm{H^+}} & \dfrac{3y\mathrm{Cl^-}}{x\mathrm{Sb_2S_3} \cdot y\mathrm{S^=}} \\ \longleftarrow & \longrightarrow \\ \text{To cathode} & \text{To anode} \end{array}$$

The ionization is not complete; it is in fact slight and the nature of the migrating ions is not quite so simple as indicated.[14] But it is not possible to make fine distinctions in a short discussion.

The gradual realization of the fact that the "impurities," e.g., the $FeCl_3$ or the H_2S, are essential parts of certain hydrosol particles, gave rise to the so-called *complex theory*, a very simple statement of the complex nature of certain colloids.

While the complex theory was accepted for many colloidal dispersions, hydrosols of noble metals such as gold and platinum were thought to be exceptions since it was believed that they could be prepared by electrically arcing these metals under pure water. This was disproved by Beans and Eastlack,[15] who demon-

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[13] These formulas give too simple a picture and are likely to mislead. For instance, the iron oxide sol written as $x\mathrm{Fe_2O_3}y\mathrm{FeCl_3}$ may give the idea that all the $FeCl_3$ is free to ionize in solution or that just the Fe^{+++} is adsorbed. For academic purposes a better simplified picture is $(x\mathrm{Fe_2O_3},\ w\mathrm{H_2O},\ y\mathrm{FeCl_3}z\mathrm{Fe^{+++}})3y\mathrm{Cl_3}^-$, where y is smaller than x, and z is very small in comparsion with y. Private communication from Dr. Arthur W. Thomas.

[14] See J. Duclaux, *J. chim. phys.*, **7**, 405 (1909).

[15] Beans and Eastlack, *J. Am. Chem. Soc.*, **37**, 2667 (1915).

strated that colloidal platinum could be formed in pure water due to the fact that platinum oxidizes in the arc thus generating an electrolyte which became part of the dispersed phase. Gold was shown to require the presence of minute amounts of certain salts, in fact those which form stable chemical compounds of gold.

It is therefore not difficult to see the origin of the solubility forces, since insoluble substances in colloidal solution are actually a part of a complex aggregate containing a soluble component. Evidence for *solution* forces as the reason, or at least one of the reasons for colloid solution stability has been given by Thomas and Frieden.[16] A simple experiment may be cited. Addition of alcohol followed by ether to a hydrosol of $x\text{Fe}_2\text{O}_3 \cdot y\text{FeCl}_3$ did not affect it. Alcohol promptly precipitated a hydrosol of $x\text{Fe}_2\text{O}_3 \cdot y\text{Fe}_2(\text{SO}_4)_3$. Ferric sulfate is insoluble in alcohol.[17]

Coagulation. In general, the addition of an electrolyte to a colloid suspension will cause coagulation. If the colloid particles are negatively charged, the coagulating agent may be either positive ions or positive colloids. If a little sodium chloride solution is added to arsenious sulfide sol the positive sodium ions neutralize the negative charges on the sulfide particles and coagulation takes place. Also, when a positive sol, say ferric hydroxide, is mixed with arsenious sulfide sol, precipitation takes place. This is called mutual precipitation, since the particles in both sols are coagulated. Another illustration of mutual precipitation is the coagulation of albumin (a positive colloid) by metaphosphoric acid (a negative colloid).

Upon examination of colloidal suspensions under the ultramicroscope it will be observed that the particles do not come in contact with one another, although they are constantly moving about in the liquid. If, however, we add a small quantity of an electrolyte the particles will be seen to approach one another and unite to form aggregates. Much work has been done determining the minimum amount of different electrolytes which will just produce coagulation in a given sol. The coagulation point has been arbitrarily defined as the point where a change in color takes place, where there is one, or where partial or complete precipitation of the disperse phase takes place **within a specified time.** If the measurements are carried out under the same conditions, compara-

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[16] Thomas and Frieden, *J. Am. Chem. Soc.*, **45**, 2522 (1923).

[17] Thomas, *J. Chem. Education*, **2**, 323 (1925); see also, Yoe, "Photometric Chemical Analysis," Vol. I, p. 96, John Wiley & Sons, New York, 1928.

ble results may be obtained. The early workers in this field are Schultze, Linder and Picton, Hardy, and Freundlich. The results of their investigations may be summed up as follows:

1. Coagulation is produced by that ion of the electrolyte which carries an electric charge opposite to the one on the disperse phase. The majority of suspensoid sols are negatively charged and, hence, the coagulating ion is the cation.
2. The concentration of the electrolyte required to cause coagulation is lower, the higher the valence of the precipitating ion. The concentration decreases very much more rapidly than the valence increases.
3. A certain minimum concentration of electrolyte must be reached before any coagulation takes place.
4. The coagulating ion is carried down by the precipitate or coagulum. When different ions are used, equivalent weights of each are always carried down by the coagulum.

An examination of experimental data on the relation between valence and the precipitating power of various ions shows that ions of the same valence have approximately the same coagulating power and also that the concentration of univalent ions required to produce precipitation is about 70 times higher than that of bivalent ions, and about 570 times greater than that of trivalent ions. If the coagulating concentrations of the ions be represented by C_1, C_2, and C_3, respectively, for univalent, bivalent, and trivalent ions, we may write the equation—

$$C_1 : C_2 : C_3 = (8.3)^3 : (8.3)^2 : 8.3$$

where the index represents the valence of the ion.

$$(8.3)^3 = 573, \quad (8.3)^2 = 69$$

This empirical relation was observed by Schultze and by Hardy. The constant varies greatly among the different sols and at best can be taken only as a rough approximation. The general expression is

$$C_1 : C_2 : C_3 = K^3 : K^2 : K$$

So far, we have not mentioned the effects of concentration and degree of dispersity of the sol on the concentration of the electrolyte required to cause coagulation. The information regarding the effect of concentration of sol is very limited. Most of the work on this subject has been done by Freundlich. His results indicate that **the electrolyte concentration increases with, and is approximately proportional to, the concentration of disperse phase.** Experiments on the second point have been made chiefly by Sven Odén. He devised methods of obtaining sulfur sols of uniform particle size and of widely different degrees of dispersion. Sols made in the usual way, as a rule, contain particles of different sizes. Odén found that, for equal concentration by weight of disperse phase, the **concentration of electrolyte required to produce coagulation increases with decreasing size of the particles**; i.e., **the higher the degree of dispersity the greater the stability of the sol.**

The phenomena of coagulation are very varied. They may be summed up under the following heads:

1. The action of electrolytes on suspensions: (*a*) adsorption, (*b*) stabilizing of ions, (*c*) valence rule, etc.
2. The " complex " theory of colloids.
3. The action of reagents on emulsoids.
4. Protection of suspensoids by emulsoids.
5. Mutual precipitation of sols.

The Adsorption Theory of the Electric Charges on the Suspended Particles of a Sol. The adsorption theory attempts to explain the electric charges on the suspended particles of a sol as being due to the adsorption of hydrogen ions or hydroxyl ions. Furthermore, since hydroxyl ions are more readily adsorbed than hydrogen ions, it follows that most sols are negative to water. Taylor[18] says, "It is not so clear why OH^- is less readily adsorbed than H^+ by those basic hydroxides which form positive sols, nor why albumin adsorbs both ions equally." The author does not agree with Taylor, for it seems to him that we should expect basic hydroxides to adsorb hydrogen ions on account of their **basic** character. Likewise, albumin being a **neutral** substance, we should expect it to adsorb hydrogen ions and hydroxyl ions about equally. Freundlich has a theory that the positive charge on basic substances is due to the hydroxyl ion having a greater diffusion velocity than the other ions present and, hence, diffuses into the dispersion medium leaving the particles positively charged; and similarly with the weakly acidic substances and hydrogen ions. This may be true, but such an assumption does not seem necessary.

[18] *Op. cit.*, p. 91

In the following table some of the more common colloids are classified according to the electric charge their particles carry in aqueous suspension.

TABLE XVIII

ELECTRICAL CHARGES OF HYDROSOLS

Electropositive	Electronegative
Metallic hydroxides	All metals
Methylene blue	Metallic sulfides
Methyl violet	Sulfur, selenium, tellurium
Bismarck brown	Silicic acid, stannic acid
Hemoglobin	Gamboge, starch
	Indigo, eosine
	Aniline blue
	Molybdenum blue

Electroendosmosis. Electroendosmosis is the movement of a liquid across a diaphragm or through a capillary tube towards one of the electrodes when an electric current is passing. This phenomenon was observed by Reuss many years ago. When a current of electricity is passed through a weak electrolyte contained in a porous cell there is a difference in the level of the liquid on the two sides of the cell. Wiedemann[19] investigated this and found that under comparable conditions the difference in level depended on two factors: (1) the applied e.m.f., and (2) the viscosity of the solution.

The electroendosmosis effect may be measured by arranging the experiment so that there is no difference in level, the liquid forced through the diaphragm being run off by a side-tube and measured, the time being noted at unit intervals. The equation for the **volume** of liquid transferred is

$$V = \frac{q\epsilon ED}{4\pi\eta l}$$

where q = area of diaphragm (or tube).
ϵ = potential difference of double layer.
E = e.m.f. at the electrodes.
D = dielectric constant of the liquid.
η = viscosity of the liquid.
l = distance between the electrodes.

The equation shows that the volume of liquid transferred is

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[19] *Pogg. Ann.*, (ii) **87**, 321 (1852).

directly proportional to (1) the area of the diaphragm (or cross-section of the capillary), (2) the potential difference between the liquid and solid, (3) the drop in potential between the electrodes, and (4) the dielectric constant; and inversely proportional to (1) the viscosity of the liquid and (2) the distance between the electrodes.

Instead of letting the liquid escape, the **pressure** may be allowed to rise. Then the equation becomes

$$P = \frac{2\epsilon ED}{\pi r^2}$$

where r = radius of the tube.

In tubes of the same material, the **height** to which the liquid will rise is directly proportional to the applied e.m.f. and inversely proportional to the square of the radius of the capillary.

Cataphoresis. Linder and Picton [20] were the first to observe that the dispersed particles in a sol migrate to one electrode or the other when an electric current is passed through the sol. They observed that the particles in ferric hydroxide sol migrate to the cathode, while those in arsenious sulfide sol go to the anode. Many sols have since been investigated. In positive sols the particles go to the cathode; in negative sols, to the anode. These results are in agreement with those of electroendosmosis.

The **velocity** of migration of the particles in a sol under the influence of an electric current is given by the following equation

$$\omega = \frac{\epsilon HD}{4\pi\eta}$$

where ω = velocity.
H = potential drop (volts per centimeter).

Adsorption. When we use the term **adsorption** in its most general sense we mean that at the boundary between two heterogeneous phases there is an unequal distribution of the substances. This boundary between two heterogeneous phases is called the **interface,** and between a solid and a gas or vapor the unequal distribution is termed gas adsorption, because the difference in distribution of the solid phase is so small as to escape observation. Similarly, where one phase is liquid and the other gas there is unequal distribution at the interface. And finally, in the systems solid-liquid (especially solutions) we have unequal distribution at

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[20] *J. Chem. Soc.*, **61,** 148 (1892).

the interface, but here too the difference in concentration is mainly on one side of the interface, i.e., the liquid side. It is often said that in solid-liquid systems the liquid is adsorbed by the solid. The reason for this is that the layer in which concentration difference exists is very thin, it wets the solid and remains sticking to the solid when the bulk of the liquid is poured off.

"Since the surface concentration differs from the volume concentration, any considerable extension of surface in a fixed volume of solution, such as occurs when a quantity of solution is shaken up with a very fine powder, must produce a very considerable change in the volume concentration."[21]

That an enormous surface in comparison with the volume of at least one of the phases is the outstanding prerequisite for adsorption, and, hence, that the main features of adsorption can be predicted, may be seen from the summary of the general phenomena of adsorption given in the next section. The relation between volume and surface in a cube is shown in the following table:

TABLE XIX

Edge Length		Number of Cubes Occupying a Volume of 1 $\overline{\text{cm}}.^3$	Total Surface
1 cm.		1	6 $\overline{\text{cm}}.^2$
0.1 cm.		10^3	60 $\overline{\text{cm}}.^2$
0.01 cm.		10^6	600 $\overline{\text{cm}}.^2$
0.001 cm.	(The diameter of a human blood corpuscle is about 0.0007 cm.)	10^9	6,000 $\overline{\text{cm}}.^2$
1 μ	(=0.001 mm.; diameter of a small coccus)	10^{12}	6 m.^{2}
0.1 μ	Limit of visibility with best microscope (×2250) is 0.14 μ (Bredig)	10^{15}	60 m.^{2}
0.01 μ	(Limit of ultramicroscopic visibility)	10^{18}	600 m.^{2}
1 mμ	(=1 millionth of a millimeter) (The diameter of the finest colloidal particles; limit of ultrafiltration)	10^{21}	6,000 m.^{2}
0.1 mμ	(Diameter of elemental molecules)	10^{24}	60,000 m.^{2}

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[21] Taylor, *op. cit.*, p. 247.

Summary of the General Phenomena of Adsorption. 1. In solutions the surface excess is, as a rule, positive. These solutions give rise to positive adsorption; i.e., if a finely divided insoluble substance is shaken up with the solution, the volume concentration in the latter diminishes.

2. The surface excess may be very large, although the solution a dilute one. Surface **defect** is always small. If a dilute solution is shaken up with an adsorbent, almost all the solute may be removed by adsorption, i.e., the positive adsorption may be large. On the other hand, negative adsorption is, as a rule, so small that it is almost impossible to measure it accurately. We should always keep in mind that negative adsorption of solute is really positive adsorption of solvent.

3. Adsorption is directly proportional to total surface. That is, for any given adsorbent of approximately uniform size, about the same amount of adsorption will be found per unit weight of adsorbent. It must be remembered that all efficient adsorbents have, in addition to "outer" surface, an enormous surface due to porosity. Hence, it is not sufficient to screen the particles of adsorbent carefully in order to obtain uniform surface. In addition to screening, or other means of obtaining uniform size of particles, the adsorbent must be prepared in such a way as to insure approximately uniform porosity.

4. Adsorption is an equilibrium. This is shown by the fact that a constant amount is adsorbed for a given weight of adsorbent (having the same total surface) regardless of whether the adsorption is first carried out in a concentrated solution and then diluted to a definite concentration, or the adsorbent placed at the start in the dilute concentration. Of course, in either event, sufficient time must be allowed to insure equilibrium. The initial velocity of adsorption is extremely rapid, frequently 90 per cent or more of the total adsorption taking place in a few seconds, while the last 1 or 2 per cent often requires a long time.

5. The total or specific surface of an adsorbent is not known. Moreover, it cannot be determined by the size of the particles. See 3 above. "It is a well-established empirical rule that the order of efficiency of adsorbents is comparatively independent of the nature of the adsorbed substance and of the solvent, and is not obviously related to the chemical nature of the adsorbent."[22]

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[22] Taylor, *op. cit.*, p. 250.

Freundlich was the first to deduce the relation between the amount adsorbed and the equilibrium concentration. He tested it experimentally with a varied and large amount of work. If we let x be the quantity adsorbed, m the quantity of adsorbent, and C the end or equilibrium concentration in the liquid (after adsorption), this relation takes the following form:

$$\frac{x}{m} = aC^{1/n}$$

where a and n are constants. The values for a and n depend on the nature of the adsorbent and the solution. The curve corresponding to this equation was called by Freundlich the " adsorption isotherm," but it is not correct to apply such an expression to adsorption equilibrium for the reason that a whole series of " adsorption isotherms " may be obtained, depending upon variations in the amount of adsorbent or variations in its specific surface. The expression " concentration function " is much better and is now generally used.

The formula is frequently called an "exponential" equation. This is incorrect. An exponential equation contains one of the **variables** (here x and C) as exponent, whereas the exponent of the concentration function is a **constant.** This constant varies within fairly narrow limits for the most widely different solutes. The value for n usually lies between 2 and 10.

6. "Adsorption should depend largely on the solvent." If the surface tension of the solvent is small, then decrease in surface tension in the solution is small. Hence, adsorption is stronger in water solutions than in alcohol. A number of empirical rules may be deduced from the theory that adsorption should depend largely on the solvent. A summary of these deductions is given in Taylor's "Chemistry of Colloids," p. 251.

The Concentration Function or So-called Adsorption Isotherm. Adsorption may be taken as a special case of Nernst's distribution law or partition law, which is expressed mathematically by the equation

$$\frac{C_1}{C_2} = K$$

in which C_1 and C_2 represent the concentration of the solute in the two layers of immiscible liquids. The equation states that the ratio of the concentration is a constant, independent of the amounts of solute and of the two liquids. The expression holds provided the molecular weight of the solute is the same in both solvents. When it is not the same, i.e., when it is associated in one and not the other, or associated in both but to different degrees, the equation takes the form

$$\frac{C_1}{C_2{}^n} = K$$

where n is the association factor.

The Preparation of Colloids. We have already said that any substance is in a colloidal state when it is sufficiently finely divided, namely, when the diameters of the particles range between 0.1 μ and 1 mμ. It is within this range that certain characteristic phenomena exhibit themselves. These phenomena differentiate matter in the colloidal state from matter in a coarse state of division on the one hand, and from matter in molecular or ionic division on the other hand. Matter in the colloidal state, therefore, occupies an intermediate position. It is at once apparent that we may approach the colloidal state (or dimensions) by starting either with coarse particles and breaking them down into smaller ones, or with molecules or ions and building them up into larger particles. To illustrate, if we drop some solid crystals into a liquid in which they are soluble, the crystals become smaller and smaller until they finally disappear, i.e., dissolve. Now, they must have passed through the colloid dimensions and, hence, it is only required that we find some means of arresting the further **decrease** in size, i.e., arrest solution of the crystals at the appropriate time, in order to obtain the substance in the colloidal state. Such methods of preparation are called "solution" methods. It is not always easy to arrest further solution of the crystals when they reach the colloid state, but theoretically, at least, it is possible.

If, on the other hand, we start with the substance in the form of molecules or ions in solution or vapor and cause the molecules or ions to combine to form crystals or aggregates we soon reach the colloidal state, but here our problem is to find some means of arresting further **increase** in size of the particles. Such methods are called "crystallization" or "condensation methods."

All the known methods of preparing colloids come under the above two heads. Although the "electrical" dispersion methods are really crystallization or condensation methods, it will be convenient to treat them as a separate group. The following classification and the illustrations are based largely upon those given in Taylor's "Chemistry of Colloids."

A. Crystallization Methods

1. Cooling a solution. Example: when a 0.02 per cent solution of sulfur or phosphorus in alcohol is cooled in liquid air a clear, glass-like, highly dispersed solid sol is obtained.

2. Replacing one liquid by another. This method depends upon the fact that, if a solvent is replaced by a liquid in which the dissolved substance is insoluble, the solute precipitates out in a highly dispersed condition. Example: gum mastic is soluble in alcohol and ether but insoluble in water. Hence, if a dilute solution of gum mastic in alcohol is added a little at a time to a large volume of water, and with constant stirring, the gum suddenly precipitates in a finely divided condition.

3. Reduction methods. Example: Zsigmondy's gold sol by reduction with formaldehyde. About 125 ml. of distilled water is heated to boiling, 2.5 ml. gold chloride solution (6 g. $HAuCl_4 \cdot 3H_2O$ per liter) and 3.5 ml. potassium carbonate solution (0.18 N) being added during the heating. When the solution begins to boil, add a little at a time and fairly rapidly, about 4 ml. of formaldehyde solution (0.3 ml. commercial formalin in 100 ml. of water). The solution should be constantly stirred with a hard glass rod during the addition of the formaldehyde. A bright red sol is obtained in a few minutes.

4. Oxidation method. The oxidation of hydrogen sulfide to sulfur and water is the only known example of this method. The hydrogen sulfide may be oxidized either by air or by sulfur dioxide.

5. Hydrolysis methods. Example: a sol of aluminum hydroxide is obtained by heating a dilute solution of aluminum acetate solution (not more than 0.5 per cent $Al(OH)_3$) in a sealed vessel at 100° C. for 10 days. The liquid is then boiled in an open vessel till all acetic acid is driven off, the water being replaced at frequent intervals.

6. Precipitation methods. Examples: (*a*) Electrolyte-free sols such as arsenious sulfide sol by the reaction between arsenious acid and hydrogen sulfide.

(*b*) Sols containing electrolytes, for example, silicic acid sol, by the reaction between sodium silicate and dilute hydrochloric acid.

(*c*) Sols with a protective colloid present such as sulfide sols of silver or cadmium with gum arabic or casein as protective colloids.

B. Solution Methods

Graham observed that certain substances could be disintegrated into colloid particles by the action of an added agent, such as water or sodium hydroxide. He termed the process " peptization." Various substances are employed as peptizing agents, namely: colloids, ions, liquids, mixed solvents, non-electrolytes, and salts. Peptization is a typical example of the solution method. Examples:

1. Sols of boron, silicon, and zirconium. An oxide of the element is mixed with potassium and heated to red heat. This reduces the oxide. The fused mass is washed with pure water until the filtrate runs through colored. Continued washing gives the sol.
2. Ferric hydroxide sol. Saturate a solution of ferric chloride with freshly precipitated ferric hydroxide and dialize.
3. Aluminum hydroxide sol. A dilute solution of aluminum chloride or nitrate is precipitated hot with dilute ammonium hydroxide, the precipitate washed and suspended in a large volume of water (200–300 ml.). The mixture is heated to boiling and 0.05 N HCl added drop by drop, with constant stirring.
4. Cadmium sulfide sol. Pass hydrogen sulfide into an ammoniacal solution of cadmium sulfate, wash the precipitated cadmium sulfide, and suspend it in pure water. Then pass in hydrogen sulfide until the precipitate disperses. Finally boil off the hydrogen sulfide.
5. Barium carbonate in methyl alcohol. A solution of barium oxide in methyl alcohol is treated with a stream of carbon dioxide. A thick gel of barium carbonate forms at first, but this disperses when more carbon dioxide is passed into it.

C. Electrical Dispersion Methods

There are two kinds of electrical dispersion methods: (1) cathode dispersion, and (2) dispersion in an electric arc between two metallic electrodes dipped in the dispersion medium. The former method was used by Ritter and by Davy more than a century ago; the latter method is due to Bredig (1898) and is by far the more important. Svedberg has modified and extended the Bredig method to the preparation of organo-metallic sols.

Bredig's Method. The apparatus consists of an ammeter, a rheostat, and two electrodes (1 mm. in diameter) of the metal to be dispersed. A solution of 0.001 N potassium hydroxide is placed in a wide, shallow glass vessel and the electrodes immersed. Upon momentarily touching the electrodes and then pulling them apart a cloud of metallic vapor is given off. This vapor condenses to give the metal sol. A current strength of 5 to 10 amperes and a voltage between 30 and 110 are used.

Svedberg's Method. In Svedberg's apparatus the secondary terminals of an induction coil (12–15 cm. spark) are connected with the electrodes, and in parallel with a condenser. The electrodes dip into the liquid contained in a wide glass vessel. At the bottom of the vessel are placed small pieces of the metal to be disintegrated. Dispersion is very rapid, and many sols can be prepared in this way. The electrodes need not be of the same metal as the one being dispersed.

APPENDIX

QUALITATIVE ANALYSIS BY DRY METHODS

Usually qualitative analyses are made by wet methods, i.e., by reactions between substances in solution. When substances are tested in the solid form, the methods are often referred to as "dry" methods. These methods include: (1) the open-tube test, (2) the closed-tube test, (3) the flame test, (4) the bead test, and (5) the blowpipe test. Dry methods are all very simple and may be performed in the field conveniently. Hence, these methods are generally employed by the mineralogist and the geologist for the examination of rocks and minerals.

In making an **open-tube test,** a small amount of the solid powder is placed in a hard glass tube (about 8 inches long and 1/4 inch inside diameter) about one-third from one end. The tube is placed in a sharply inclined position with the powder nearer the lower end and gently heated, first at the upper end and then at a point just above the sample or sometimes directly beneath the sample. Under such conditions the powder is heated in a steady current of air which passes up the tube and will be oxidized if such a reaction is possible. Various oxides may come off and either condense upon the upper walls of the tube or escape. The oxides may be recognized by their color or odor or both. For example, sulfur or sulfides give off sulfur dioxide, arsenic compounds yield arsenious oxide which condenses to small colorless octahedral crystals, molybdenum may be recognized by a deposit of pale yellow to white crystals, mercury minerals give a deposit of minute globules of metallic mercury, etc.

The **closed-tube test** is made by placing a small quantity of the powdered material in the bottom of a soft glass tube (about 4 inches long and 3/16 inch inside diameter) which is closed at one end. The tube is then heated at the bottom over a Bunsen flame. Under this condition the powder is heated almost out of contact with air and may simply undergo decomposition into simpler substances. For example, water of crystallization is driven off and condenses to drops of water on the upper cold end of the tube, all sulfides which contain an excess of sulfur give a sublimate of yellow sulfur (red when hot), native arsenic and some arsenides produce a shiny deposit of metallic arsenic, etc.

A number of the elements impart characteristic colors to the flame when their salts or minerals are heated in the flame of a Bunsen burner. The **flame test** is best made by placing a little of the powdered substance (preferably moistened with hydrochloric acid) in a small loop on the end of a platinum wire and then heating it in the edge of the Bunsen flame. Sodium salts and its minerals give an intense yellow flame; potassium gives a violet colored flame; strontium and lithium color the flame crimson; calcium produces an orange flame; barium, boron, and molybdenum give a yellow-green flame; copper produces an azure-blue flame (the oxide gives an emerald-green flame), and zinc a bluish-green.

Bead tests are made by fluxing a small amount of the powdered material with borax or sodium ammonium hydrogen phosphate ("microcosmic salt"). A clear glass bead of the flux is first made by heating some borax or microcosmic salt in a small loop on the end of a platinum wire. The hot bead is then touched to some of the powdered sample, a little of which adheres to the bead, and the mixture fused in the flame. Both oxidizing and reducing flames should be tried, as some beads differ in color depending upon the type of flame used for fluxing. The bead should also be examined both hot and cold. In Table XX is listed a few of the metals and their color reactions with the fluxes.

Several **blowpipe tests** are important aids in the identification of minerals and salts. For example, the fusibility may be obtained by heating a small fragment of the substance in the blowpipe flame just beyond the tip of the inner cone, where the temperature is the hottest. Note whether or not the substance is fusible. If fusible, note the ease with which it fuses. Another blowpipe test consists in roasting a little of the powdered material spread thinly on a stick of charcoal (about 4 inches long, 1 inch wide, and ½ inch thick). Heat only at a dull red heat, keeping the blue tip of a small oxidizing flame a considerable distance away. Drive off any volatile constituents, mix the residue with a little powdered charcoal, and repeat the roasting. Observe the color and character of the sublimate on the charcoal. Also note any odor or flame coloration. For example, arsenous oxide is very volatile, is white to grayish, and often has a strong garlic odor. Zinc oxide is canary yellow while hot, white when cold, is non-volatile in the oxidizing flame, and when moistened with a drop of cobalt nitrate solution and ignited, the sublimate becomes green.

TABLE XX

Oxides of	Borax Bead		Sodium Metaphosphate Bead	
	Oxidizing flame	Reducing flame	Oxidizing flame	Reducing flame
Chromium	Hot: yellow	Green	Dirty green	Dirty green
	Cold: yellowish green	Green	Fine green	Fine green
Copper	Hot: green	Colorless to green	Green	Brownish green
	Cold: blue	Opaque red	Blue	Opaque red
Cobalt	Hot: blue	Blue	Blue	Blue
	Cold: blue	Blue	Blue	Blue
Nickel	Hot: violet	Opaque gray	Reddish to brownish red	Reddish to brownish red
	Cold: reddish brown	Opaque gray	Yellow to reddish yellow	Yellow to reddish yellow
Manganese	Hot: violet	Colorless	Grayish violet	Colorless
	Cold: reddish violet	Colorless	Violet	Colorless

Certain metals (e.g., lead, silver, copper, etc.) may be reduced from their minerals or salts by heating a little of the powdered material on charcoal with the blowpipe. Mix equal volumes of the finely powdered substance, powdered charcoal, and borax

TABLE XXI

DUNNINGTON'S TABLE FOR DETECTION OF METALLIC ELEMENTS IN SIMPLE COMPOUNDS BY BLOWPIPE EXAMINATION

(EXCEPTING COMPOUNDS OF Ba, Sr, Ca, Mg, with SiO_2 or P_2O_5)

Apply following tests in the order indicated, noting results:

Gradually heat on charcoal a little of the substance (S) until no further change occurs

NOTE:

1.—It disappears:—If necessary, also heat S on mica.

Note:

11.—Volatilizes (except traces):—In tube put S with 12 parts soda and charcoal, heat gently to *dry it*, then to red heat.

Note:

A

- (*a*)—Vapor alkaline to most litmus paper .... Ammonium
- (*b*)—Sublimate of metal globules .... Mercury
- (*c*)—Sublimate of metal ring (garlic odor) .... Arsenic
- (*d*)—Sublimate other than As or Hg, add KCN (or try test 2′) .... Repeat 11
- (*e*)—No sublimate and no alkaline vapor ...... (or try test 2′) .... No base

12.—Readily fusible:—Pass on to test 21.

2.—There is a residue:

Note:

21.—Not a metal:—Put ignited mass on moist litmus paper.

Note:

211.—Strongly alkaline (and white):—Heat S(+HCl) on platinum wire.

Note:

B

- (*a*)—Flame brilliant yellow and S is *fusible* .... Sodium
- (*b*)—Flame pale violet (through blue glass crimson) and S is *fusible* .... Potassium
- (*c*)—Flame red orange (through blue glass gray) .... Calcium
- (*d*)—Flame crimson (compare with foregoing) .... Strontium
- (*e*)—Flame apple green (seen on *fine* wire, when very hot) .... Barium
- (*f*)—Flame not colored or indistinct .... Magnesium test 1′

212.—Not alkaline (or slightly alkaline from traces of metals B).

Note:

1′.—Infusible *and* white residue:—Moisten with cobalt solution and re-ignite.

Note:

C

- (*a*)—Blue mass and *infusible* .... Aluminum
- (*b*)—Green mass .... Zinc test 2′
- (*c*)—White mass (sometimes pinkish) no base, or if 211 (*f*) .... Magnesium
- (*d*)—Greenish blue or indistinct .... See test 2′

2′.—Fusible *or* colored residue:—On charcoal fuse S with 4 parts soda and charcoal. If not fused readily, add a lump of KCN and re-fuse.

Note:

2′1′.—No metal bead.

Note:

2′1′1′.—A coating on the charcoal.

Note:

D

(*a*)—White, yellow when hot . . . . . Zinc

(*b*)—Yellow brown, very volatile . . . . . Cadmium

2′1′2′.—No coating:—Fuse S in borax bead, and heat in oxidizing flame.

E

Note: *hot.*	*cold.*		
(*a*)—Blue	Blue		Cobalt
(*b*)—Green	Blue	See test 221	Copper
(*c*)—Green	Green	Colors bead of soda yellow	Chromium
(*d*)—Purple	Violet	Colors bead of soda green	Manganese
(*e*)—Purple brown	Pink brown	Colors bead of soda gray	Nickel
(*f*)—Orange	Yellow	(Ignited residue is magnetic)	Iron
(*g*)—	Indistinct	Reheat in oxidizing flame	

2′2′.—A metal bead:—Pass on to next.

22.—A metal bead:—Hammer it gently. (For a larger bead, if needed, fuse S with soda and KCN.)

Note: *Color.*

221.—Red. (Hard, malleable) . . . . . Copper

222.—White:—Heat the *metal* bead on charcoal.

Note:

1°.—Malleable:

Note:

1° 1°.—A coating.

Note:—Color.

F

(*a*)—Yellow (white outside) (Metal, soft) . . . . . Lead

(*b*)—White (close to assay) (Metal, hard) . . . . . Tin

1°2°.—No coating or faint brown. (Metal, hard) . . . . . Silver

2°.—Brittle:

Note:—Color of coating.

(*a*)—White (very volatile) . . . . . Antimony

(*b*)—Yellow. (Metal, less brittle) . . . . . Bismuth

To examine complex compounds, apply severally the distinguishing tests for each of the above groups of elements: A, B, C, etc.

with three volumes of soda. Moisten the mixture with water and place a little of it in a shallow depression on one end of the charcoal stick. Fuse the mixture in a strong reducing flame for several minutes, unless a metal bead appears in a shorter time. If no metal is visible, remove the mass along with a little of the charcoal next to it, and grind it in an agate mortar, while a slow stream of water is run into the mixture to carry away the charcoal powder and the excess soda. Any globules of metal present will be flattened by the grinding and can be detected on the pestle and in the mortar. If the metal is white, it may be tin, lead, silver, platinum, etc. The metal may be transferred to a watch glass and treated with a drop or two of nitric acid, warmed gently, and diluted with a drop of water. Metallic tin is changed to white, insoluble stannic oxide; lead dissolves and gives a white precipitate of lead sulfate with a drop of dilute sulfuric acid; silver is soluble and forms a white precipitate of silver chloride with a drop of dilute hydrochloric acid, the precipitate dissolving upon the addition of ammonium hydroxide; platinum is insoluble in the nitric acid but soluble in *aqua regia.* A yellow or red metal may be copper or gold. Copper dissolves in nitric acid and gives a reddish-brown precipitate with potassium ferrocyanide; gold is insoluble in nitric acid but soluble in *aqua regia.* The presence of gold may be confirmed by evaporating the *aqua regia* solution just to dryness, dissolving the residue in a few drops of water, and then adding a drop of dilute stannous chloride solution. A violet-brown precipitate confirms the presence of gold.

In Table XXI is given an outline for the detection of metallic elements in simple compounds by means of blowpipe tests.

THE SCALE OF HARDNESS

The **hardness** of a substance is its power to resist penetration of its surface by another substance. The relative hardness of two substances may be determined by finding out which will scratch the other when the surface of one is rubbed with the edge of the other. The harder substance, of course, will scratch the softer. An arbitrary scale of hardness has been established by selecting ten minerals of varying degrees of hardness and arranging them in order of increasing hardness. Each of the minerals in the following list will scratch the surface of a specimen of any one preceding it.

1. Talc.
2. Gypsum (or rock salt).
3. Calcite.
4. Fluorite.
5. Apatite.
6. Feldspar.
7. Quartz.
8. Topaz.
9. Corundum.
10. Diamond.

TABLE XXII

Principal Composition of Some Minerals

Apatite	$Ca_3(PO_4)_2 \cdot Ca(F, Cl)_2$	Galena	PbS
Aragonite	$CaCO_3$	Gypsum	$CaSO_4 \cdot 2H_2O$
Argentite	Ag_2S	Halite	
Asbestos		(rock salt)	$NaCl$
(chrysotile)	$H_4Mg_3Si_2O_9$	Ilmenite	$FeTiO_3$
(authophyllite)	$(Mg, Fe)SiO_3$	Limestone	$(CaMg)CO_3$
(tremolite)	$CaMg_3(SiO_3)_4$	Limonite	Fe_2O_3
Barite	$BaSO_4$	Magnetite	Fe_3O_4
Bauxite	Al_2O_3	Niter	
Beryl	$Be_3Al_2(SiO_3)_6$	(saltpeter)	KNO_3
Borax	$Na_2B_4O_9 \cdot 10H_2O$	Pyrite	FeS_2
Calcite	$CaCO_3$	Pyrolusite	MnO_2
Cassiterite	SnO_2	Quartz	SiO_2
Chromite	$FeCr_2O_4$	Rutile	TiO_2
Cinnabar	HgS	Siderite	
Corundum	Al_2O_3	(spathic iron)	$FeCO_3$
Cryolite	Na_3AlF_6	Sphalerite	ZnS
Dolomite	$CaMg(CO_3)_2$	Stibnite	Sb_2S_3
Epsomite		Sylvite	KCl
(Epsom salt)	$MgSO_4 \cdot 7H_2O$	Talc	
Feldspar	$KAlSi_3O_8$	(soapstone)	$H_2Mg_3(SiO_3)_4$
Fluorite	CaF_2	Witherite	$BaCO_3$

TABLE XXIII

VAPOR PRESSURES OF WATER

t° C.	Pressure, mm. of Hg	*t*° C.	Pressure, mm. of Hg	*t*° C.	Pressure, mm. of Hg
0	4.60	14	11.91	28	28.10
1	4.94	*15*	12.70	29	29.78
2	5.30	16	13.54	*30*	31.55
3	5.69	17	14.42	31	33.41
4	6.10	18	15.36	32	35.36
5	6.53	19	16.35	33	37.41
6	7.00	*20*	17.39	34	39.57
7	7.49	21	18.50	*35*	41.83
8	8.02	22	19.66	36	44.20
9	8.57	23	20.89	37	46.69
10	9.17	24	22.18	38	49.30
11	9.79	*25*	23.55	39	52.04
12	10.46	26	24.99	*100*	760.00
13	11.16	27	26.51		

From Smithsonian Tables (1914)

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