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STRUCTURAL CHEMISTRY OF INORGANIC COMPOUNDS

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STRUCTURAL CHEMISTRY OF INORGANIC COMPOUNDS

by

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VOLUME I



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AUTHOR'S FOREWORD

This work attempts to furnish inorganic chemistry with that which organic chemistry has long possessed as a basis for its systematization, namely, a structural and constitutional theory in one embracing representation. This simultaneously points the way to a systematization of inorganic compounds, which, other than that based upon a classification according to the elements, is founded upon the properties that are governed by constitutional peculiarities. The perspective obtained thereby is quite different in nature from that which results when inorganic chemistry is treated element for element. It has not been my intention to present the whole state of knowledge of inorganic chemistry according to this alternative viewpoint. It should nevertheless become clear that a correctly drawn up inorganic structural chemistry, taken in conjunction with the organic, provides a magnificent and internally consistent over-all picture of the structure and constitution of matter.

Since, in consequence of unfavourable external conditions, I have still not been able to gain complete access to the foreign literature, and many papers are available to me in abstract form only, I would be grateful for support by the sending of reprints, as well as for having my attention drawn to omissions and errors.

The English edition differs from the German only in such additions and alterations as appeared necessary in consequence of the literature which came to my knowledge between 1947 and 1949.

My thanks are due to the translator, Dr. L. H. LONG, for the care which he has bestowed upon the translation.

Tübingen, January 1950

WALTER HÜCKEL

TRANSLATOR'S FOREWORD

In collecting the material for this new approach to structural inorganic chemistry, Professor HÜCKEL has rendered a valuable service to chemical science. The labour of translating this book has been undertaken with the firm conviction that it will prove to be of great value to the English-speaking chemist, and that its service will not be restricted to the academic student alone.

The task has confronted the translator with a number of problems, not least of which has been the unusual complexity of the original language. This has been simplified where practicable by a somewhat free translation. As further simplification would inevitably have involved shifting the Author's emphasis, I have in general considered it to be in the best interests to maintain a close adherence to the original text, that is, as far as the divergence in English and German syntax allows.

For the original title, *Anorganische Strukturchemie*, it has been necessary to find an English counterpart other than *Structural Inorganic Chemistry* in view of the recent book by A. F. WELLS bearing this title, which book did not appear in time to influence the preparation of Professor HÜCKEL's manuscript. It should be remarked that the aims and scopes of the two works are very different. The English title ultimately adopted has the consent of the Author.

Except for a few late references added in proof, all additions and amendments to the text of the first German edition have been made at the Author's suggestion or with his approval. The same also applies to the translator's notes, and apart from these the translator is not responsible for any of the views expressed in this book. In order to eliminate errors which had crept into the German edition, the thousands of references in the footnotes have been individually checked, in part by the translator and in part by Mr. J. FAHRENFORT of Amsterdam, to whom grateful acknowledgment is due. The same is also due to Professor J. A. A. KETELAAR of the Laboratory for General and Inorganic Chemistry, Amsterdam, for carefully controlling the sections on crystal chemistry and for suggesting numerous minor improvements to the text and figures, especially in respect of Chapter VIII; and lastly but not least to my wife for her unwearying assistance, without which this book could not have appeared in so short a time after the publication of the original German edition.

The English edition is being published in two volumes. The first volume comprises Book I (Chapters I, II and III) and Book II (Chapters IV, V and

VI): the second volume contains Book III (Chapters VII to X inclusive), the individual Chapters XI and XII and the index. The latter (subdivided into Author Index, Subject Index and Index of Elements and Compounds) comprises some 15,000 references to the text, and is perhaps as extensive as that for any treatise on chemistry of comparable size.

Exeter, January 1950

L. H. LONG

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BOOK I

STOICHIOMETRY AND SYSTEMATIZATION

CHAPTER I

FUNDAMENTAL PROBLEMS IN CHEMISTRY

1. The Problematical Element

The countless vain attempts of the alchemists to make gold, in addition to the chemical experience gained in the ages of alchemy and iatrochemistry and the chemical knowledge obtained through the forging of ores, all led to the recognition that not all desired transformations of matter are possible. But in the absence of a systematic investigation in order to discover which transformations actually are possible and which not, this recognition was slow in gaining general acceptance. It was about the middle of the seventeenth century when BOYLE first enunciated clearly that only a relatively few basic substances or *elements* exist, out of which other substances are compounded. But BOYLE himself did not understand how to relate his definition of the elements with experimental observation. Neither did he connect the observation that part of the air was consumed during combustion with the increase in weight obtained on calcining, of which he was also aware. Nor was he certain whether vitriol was a constituent of sulphur, or *vice versa*¹. But the recognition that basic substances exist did not by itself bring progress while the paths to their discovery were still untrodden. Furthermore, it is striking that in spite of appropriate definition, it was long before a planned search for the elements through the means of experiment got under way. This took place first in the century after BOYLE through the efforts of LAVOISIER and those investigators who extended his work. It is LAVOISIER's due that he illustrated, principally by means of combustion phenomena, the methods by which it could finally be determined what constitutes an element. This demanded not only a qualitative knowledge of material changes, but also quantitative analysis. It was LAVOISIER who first taught how to make correct use of the latter. The importance of weighing the substances involved in chemical changes had admittedly been stressed by isolated investigators long before LAVOISIER, especially by J. JUNGIUS in 1642. But these, even with the aid of the balance, failed to solve any chemical problems. It was only after the successes of LAVOISIER that the importance of the balance as a chemical instrument became generally recognized.

¹ H. KOPP, *Geschichte der Chemie* I, p. 166; A. LADENBURG, *Entwicklungsgeschichte der Chemie*, p. 7 (4th Ed., 1907).

The explanation why the concept of the element once formulated did not immediately stimulate a search for the elements themselves is to be sought in the deeply rooted preoccupation with pre-LAVOISIER theories concerning the composition of matter. It was believed, namely, that certain properties of substances are governed by their content of certain principles. For instance, sulphur was regarded as the combustible principle and, as such, was supposed to be contained in all combustible substances, while mercury passed for the metallic principle, which was likewise thought to be a constituent of all metals. In BOYLE's time, admittedly, this conception leading back to PARACELSUS and in its remotest origins still further, had already been relinquished. Nevertheless, the supposition that certain principles exist which govern the properties of the substances containing them was firmly retained, except that these principles were no longer identified with already known substances. One theory founded on these premises was the Phlogiston Theory, advanced shortly after BOYLE, which prevailed for almost a century. It was this which sidetracked research from the direct path to the discovery of the elements, and even barred the way. The Phlogiston Theory, put forward by STAHL around the year 1700, stated that all combustible substances contain phlogiston which is released on burning. It was accordingly supposed, for example, that sulphur consisted of sulphuric acid and phlogiston, and that phlogiston was contained in all oxidizable metals. It is seen that just those substances we now know to be elements appeared in many instances as phlogiston-containing compounds. The essence of truth contained in the Phlogiston Theory, and the ends which it was believed would be furthered by its help, will be investigated in a special section. Just how deeply rooted was this idea of a material combustible principle as a component of combustible substances, is apparent from CAVENDISH's taking his newly discovered hydrogen for the then unknown phlogiston, while somewhat later we find SCHEELE regarding hydrogen as, though not absolutely, still fairly pure phlogiston. It is to be seen from this instance, to which one could append others, that BOYLE's conception of an element, which LAVOISIER appropriated, signified absolutely nothing to the phlogistian chemists.

It is all the more remarkable that several elements were discovered by the phlogistians, like, for example, hydrogen in 1766 by CAVENDISH, oxygen in 1774 by SCHEELE² and also by PRIESTLEY, chlorine in 1774 by SCHEELE, and manganese in 1774 by GAHN and SCHEELE; whereas, in contrast, LAVOISIER himself was the discoverer of not a single element, although he demonstrated a number of known substances, mostly metals, to be elements. This fact teaches us that LAVOISIER's exact methods of working must have lacked something which the phlogistians possessed to a high degree. The converse

² In his book *Chemische Abhandlung von der Luft und dem Feuer* (Upsala and Leipzig, 1777) SCHEELE regarded oxygen as a phlogiston-poor compound of water with a hypothetical saltlike material. KOPP, *Geschichte der Chemie* I, p. 261.

that the latter lacked something which LAVOISIER possessed to a high degree is to be gathered from their theoretical attitude, already mentioned, towards experimental results. The phlogistians were not conscious of the import of their discoveries for chemical knowledge as a whole. So far as they gave theoretical discussions at all, these were vague and confused³.

The ultimate difference between LAVOISIER and the phlogistic age rests on the fact that LAVOISIER concerned himself essentially with the *quantities*, and the phlogistians with the *qualities* of substances, as well as the phenomena accompanying chemical change. For this reason the labours of the latter were experimentally much more copious than those of LAVOISIER. It is likely that even with his method of working LAVOISIER would have discovered oxygen eventually, but his search would certainly have been more laborious than that of PRIESTLEY, or even that of SCHEELÉ. Although LAVOISIER's mode of working and thinking did not produce such great and rapid experimental success as that of the phlogistian chemists, his kind of investigation was nevertheless absolutely necessary for guiding the development of chemical knowledge along sound paths. It was soon to be taken up by other investigators, thus opening up a highway of chemical discovery which followed the course first laid down by LAVOISIER. The ensuing elaboration of quantitative analysis by PROUT, and later to a still greater degree by BERZELIUS, existed complete in the mind of LAVOISIER. The constancy in composition of substances which followed next from the foregoing, taken as a whole, had been suspected by LAVOISIER, and, although unproved⁴, jointly accepted by many chemists as almost self-evident. This in turn led, unforeseen by LAVOISIER, to the Law of Constant and Multiple Proportions. In point of fact, the Law of Constant Proportions had already been discovered previously by J. B. RICHTER in another manner and by a line of reasoning entirely foreign to LAVOISIER (p. 20), its *universal* validity being first demonstrated by the exact analyses of BERZELIUS.

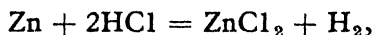
To the question, already answered by LAVOISIER: *What is an element, and how can one demonstrate in any given case the elementary nature of a substance?* a second was to be added: *What is a pure substance, a chemical compound composed of several elements?* By means of experiment, a more certain foundation for the useful definition of the concept of a pure substance and a chemical compound was obtained, upon which the chemistry of the 19th century with its language of formulae could be constructed.

This chemistry of substances of known composition, however, still lacked something. Their composition, as expressed in formulae, was empirical, as were also the reaction equations set out by means of these formulae. In other words, if the elements out of which a substance is formed

³ Concerning the theoretical confusion which dominated the mind of the brilliant experimenter SCHEELÉ, an example is given by A. LADENBURG in his *Entwicklungsgeschichte der Chemie*, p. 20 (4th Ed., 1907).

⁴ From 1772, the analyses of various salts by C. F. WENZEL were available, from which the constancy of their composition followed.

were known, its quantitative composition did not follow from this. And even if one accepted the latter as given by the work of the quantitative analyst, one still did not know if and how it would react with a second substance of known composition. Only experience taught, in the next instance, that the reaction between zinc and hydrogen chloride proceeds in the sense of the equation



and not of the equation



A genuine "chemical feeling" for the manner in which two substances interact could be obtained only by experience. Consequently the beginner who had not yet acquired this often made the grossest blunders. Similarly, one had to note from experience which substances were precipitated as sparingly soluble from solution. Such experience was in fact possessed by many of the chemists adhering to the Phlogiston Theory who, like SCHEELE, for example, were pure empiricists. As investigators interested principally in the *quality* of phenomena, the question concerning them was not: *What is a pure, homogeneous substance, and how is it composed?* but: *How do the substances which I can isolate by crystallization, distillation, or by other means react with each other?* Physical properties such as crystal form, solubility, and boiling point, which (as illustrated by SCHEELE's discoveries in the domain of organic acids) were recognized frequently with great clarity of perception, provided in themselves a sufficiently convincing reason for always using the same materials in different experiments, thus keeping to conditions which could be reproduced. Quantitative analysis — now constantly used as a control — was not then employed as the means of proof of purity of a substance; but since the ability to react was added by way of further differentiation, the experimentalists worked almost throughout with pure compounds, and knew how to differentiate these from mixtures. Thus SCHEELE and CAVENDISH, for instance, like LAVOISIER, recognized air to be a mixture.

The question, therefore, whether and how two substances react on being brought together was then, and even much later, theoretically completely unfathomable. The theory then current, the Phlogiston Theory, instigated solely the collection of observations concerning combustion phenomena and their classification according to a particular conception. In this manner it was attempted to clothe the above-named question in a hypothetical garb which, superficially at least, satisfied the mind. This was all the simpler, as to achieve it necessitated only a slight modification of a hypothesis already put forward by EMPEDOCLES. One spoke of a *chemical affinity* which either drove substances to combine with one another, or caused the regrouping of their component parts in an exchange reaction.

The efforts of the chemists who were not content with experimental determinations were now directed to the construction of affinity tables from which reactions to be expected could be read off. This completely unclarified conception of chemical affinity did not for one moment possess a physical background, but was anchored in the spiritual world of human perceptions. In this we see today the reason why nothing logical normally came out of it, although sometimes, without doubt, correct beginnings were contained in these tables dealing with the order of phenomena (pp. 28, 29). There remained, however, more than half a century before BERTHOLLET in his *Essai de Statique Chimique* in 1803 was to reduce the affinity tables to an absurdity, and pave the way, at least, for a more logical framing of the concept of affinity. But he too did not succeed in elucidating the concept sufficiently clearly for reasons which will be discussed later.

The quest for the cause of chemical processes, which came to be termed chemical affinity, thus existed in the forefront of the minds of the chemists working and thinking qualitatively before those working quantitatively enquired into the composition of matter. The first enters into the very nature of chemical processes, while the quest for the composition contents itself with the actual substances prepared by chemical operations. Yet the latter had to be satisfied before one could even think of going about the former. When it was realized that, in consequence of the limitation hereby imposed, something was lacking in the chemistry of LAVOISIER and in the chemistry of substances of known composition developed from it, it was simultaneously perceived that attention was being directed to the next attainable and clearly recognizable objective.

But since the problem of chemical affinity was older than that of composition, a deep division extended in the presentation of chemistry throughout approximately a century. It was usual to commence with chemical affinity, even though the concept was not to any extent clearly outlined and neither the question of its measurement nor that of its cause could be answered in anything like a satisfying manner. Only then did the stoichiometric laws follow, laws which could be exactly formulated and rigidly proved by experiment, in effect, "the chemistry founded by LAVOISIER". Thus the advancement in chemical knowledge by the shaping of clear ideas and experimental objectives was in this manner relegated to the background in favour of a still unsolved and therefore not clearly definable problem. But apart from this, it did not appear possible to combine into a single unified plan the investigations on stoichiometry, including structural theory, with those on the doctrine of affinity. To comprehend the entire problematical element in chemistry, therefore, it is necessary to follow separately the historical development of both points of inquiry, and thus in course of time become familiar with the knowledge gained from the two different viewpoints.

The dualism in the development of chemical research was first clearly demonstrated by VAN 'T HOFF during the 1904 world exhibition in St.

Louis, who, in an address, distinguished the two lines of development by the names of the foremost investigators adopting them. In the ensuing discussion, OSTWALD completed the lists ⁵ by the addition of the names of RICHTER and WENZEL.

Stoichiometry and Atomistics

RICHTER 1792

LAVOISIER, DALTON
 GAY-LUSSAC, AVOGADRO
 DULONG, PETIT, MITSCHERLICH
 FARADAY
 BUNSEN, KIRCHHOFF
 The Periodic System
 PASTEUR, Stereochemistry
 RAOULT, ARRHENIUS
 Radioactivity (BECQUEREL, CURIE)

Theory of Affinity

WENZEL 1777

BERTHOLLET, GULDBERG, WAAGE
 BERZELIUS ⁶, HELMHOLTZ
 MITSCHERLICH, SPRING
 DEVILLE, DEBRAY, BERTHELOT
 THOMSEN, BERTHELOT
 HORSTMANN, GIBBS, HELMHOLTZ

VAN 'T HOFF

The names RICHTER and WENZEL, which, for the sake of completion, were placed by OSTWALD at the head of VAN 'T HOFF's lists, take a special place in the history of chemical development. Although, for the precision with which they formulated their ideas, they must pass for the creators of the respective lines of thought from which proceeded the two directions of development recognized by VAN 'T HOFF, their own investigations were in point of fact denied a broader development, and no other investigator became associated with them. Both workers remained more or less forgotten, and their services to science were recognized at their full value only recently. The reason why LAVOISIER and BERTHOLLET, and not they, determined the development in the two directions is to be sought in the universality of the presentation which LAVOISIER and BERTHOLLET were able to frame. It was possible to gather from both LAVOISIER's and BERTHOLLET's presentations which fundamental questions were involved. With RICHTER and WENZEL this was not possible, since they, as experimenters, confined themselves to relatively narrow fields. But within these, as far as their mode of posing questions to Nature and their experimental solving of these were concerned, they were the universal spirits of LAVOISIER and BERTHOLLET in advance.

⁵) WILHELM OSTWALD, *Lebenslinien* II, p. 413 (Klasing, Berlin, 1927).

⁶) Intrinsically, because of his analytical work proving the Law of Constant and Multiple Proportions which resulted from DALTON's atomic theory, BERZELIUS should be included under stoichiometry and atomistics. Because of his electrochemical theory, he belongs under the theory of affinity (p. 29 ff). In addition, the classification and the inclusion or omission of some of the other names might be disputed. For further concerning the completion of VAN 'T HOFF's lists, see Chapter XII.

The development which chemistry next underwent in the nineteenth century was a step forward in the tracks which LAVOISIER had indicated, being based on reasons which, as far as they concern chemical affinity, will be explained in the discussion of BERTHOLLET's viewpoints. Hence it is possible with a certain justification in the case of nineteenth century chemistry to speak of "the chemistry founded by LAVOISIER"⁷. One must not forget here, however, that various fundamental experimental facts of this chemistry were discovered and their significance interpreted not by LAVOISIER but, independently of his thought processes, by other investigators.

Before going into the extension of chemical knowledge which found its outlet in the researches of LAVOISIER and in the stoichiometric experiments carried out in his spirit, it is necessary to show where the breach between the old and new modes of thought in chemistry actually lies. That is best attained by a critical appreciation of the Phlogiston Theory, which stands on the borderline of two chemical ages but is rooted wholly in the older views.

2. The Phlogiston Theory, its Roots and its Overthrow

A whole century was to pass from the time when BOYLE produced his definition of an element to the time when the problem of determining which substances are elements received experimental treatment by LAVOISIER. How was it that chemical knowledge could ignore a fundamental question for so long, once it had been shown to exist, and that even BOYLE did not indicate the path towards its solution? The answer is given by an analysis of the origins of that particular chemical theory which predominated almost exclusively during the hundred years from 1675 to 1775, namely the *Phlogiston Theory*. In point of fact, it was first put forward by GEORG ERNST STAHL about the year 1700. Nevertheless, its basic idea had already been evolved previously, although in a slightly different form, by JOHANN JOACHIM BECHER. Even the latter's thoughts were not original or new, but were enmeshed and rooted in yet much older thought-processes. Before the real origins of the Phlogiston Theory can be investigated, both the theory and its achievements must first be described and assessed as presented by the viewpoints of the period and of the present day.

The Phlogiston Theory assumes a combustible principle, which is named phlogiston — from φλογίζεσθαι, to burn — in every combustible substance. This is released during combustion of the substance. By this concept, theory is linked directly to observation, for during the combustion of the usual fuels, as also of sulphur and phosphorus, the material disappears in flame and smoke and with the evolution of heat and light, leaving, at the most, a small heap of ash. The success of the Phlogiston Theory did not depend, however, on the assumption which had already been made previously in a similar form, namely, of a combustible principle dispersing on com-

⁷ Hence the well-known and much-attacked sentence of A. WURTZ: "La chimie est une science française; elle fut constituée par LAVOISIER."

bustion, but — and this was at the same time the novelty of it — on the assumption that this principle, phlogiston, was not only given up, but conversely reabsorbed by incombustible substances. In this way the processes now designated by oxidation and reduction were fundamentally linked up with one another. Easily combustible substances such as carbon contain much phlogiston and can transfer this to other substances, whereupon these, as for example iron oxide which thus becomes iron, are rendered combustible. *In this linking of oxidation and reduction rests the main achievement of the Phlogiston Theory*, since it permitted these phenomena to be classified according to a common viewpoint.

STAHL's Phlogiston Theory and LAVOISIER's oxygen theory of combustion which replaced it shared the common idea, that on oxidation and reduction something is transferred from one substance to another. But apart from this similarity, the Phlogiston Theory intended in the last resort to express something very different from the oxygen theory of LAVOISIER, which alone led to a correct conception of the element. LAVOISIER regarded oxygen, which on oxidation and reduction is transferred from one substance to another, as itself a material substance. By this be understood quite consistently something which could be weighed and which, in physical terms, possessed mass. The mental connection of substance and mass was for him the essential point. With STAHL, on the other hand, as also with those who followed his teaching, it was never clearly expressed whether phlogiston was material or not. With STAHL himself one finds as many indications of the one conception as of the other. That STAHL regarded carbon, that is, a substance, as fairly pure phlogiston, gives rise to the opinion that he supported the material theory of phlogiston. On the other hand, when one considers how STAHL in his medical theories worked with unsubstantial conceptions like, for example, the *anima* as attuning and holding together the functions of life, one is tempted to believe that he also tried to identify phlogiston with an unsubstantial principle. If he did not view it as something actually material, it is immediately comprehensible why he and his disciples did not make a special search for it. With the later phlogistians, however, a tendency towards a material conception is distinctly traceable. Still without having made any attempt to discover it, they saw in hydrogen, after its discovery in 1766 by CAVENDISH, pure, or at least nearly pure, phlogiston. By regarding hydrogen as material phlogiston, it was of course possible to describe even complicated series of processes like, for example, the following: The phlogiston contained in combustible iron is released on covering it with sulphuric acid; on heating the residual iron vitriol, the sulphuric acid is recovered; the involatile iron oxide, then known as *caput mortuum*, is again transformed into combustible iron by means of the phlogiston evolved by the acid, that is, the hydrogen. That phlogiston (= hydrogen) is released without the appearance of fire on its formation from iron and acid, is ignored in this explanation, as is also the formation of water on

the reduction of iron oxide. Let it be remarked again that the search for phlogiston in no case led to the discovery of hydrogen.

In regarding phlogiston as something like a substance, a contradiction with experiment ought to have been noticed immediately the proportions by weight, then already partly familiar, were considered, and not merely the outward phenomena during combustion. The burnt metals — metal oxides, then termed metal calces — weighed more than the metals themselves. If by matter something weighable is understood — and this conception was admittedly not yet universally recognized — a material concept of phlogiston yielded in oxidation and reduction processes changes in weight of exactly the opposite sign to those observed. But, even without a material conception of phlogiston, it must have remained remarkable how substances could gain in weight when something went out from them. The gain in weight could be explained only by the oxygen theory of combustion. By including in the weight also the gaseous products of combustion which normally mingled with the air, it, supported experimentally upon the widest basis, forced the Phlogiston Theory to give way. However, this did not happen without a hard struggle. What was it that prevented so many investigators, including the leading experimenters, from following LAVOISIER's claims, and caused them to hold to the Phlogiston Theory? Surely, in the first place, the fact that with help of the latter numerous processes had been explained and set in relationship with each other; that is, the sheer impetus of conservatism which always makes itself noticeable where the relinquishing of a long-cherished theory is concerned. But there was also another important reason. The Phlogiston Theory was in harmony with the ideas of combustible substances which had been held from ancient times, whereas LAVOISIER's theory in relation to these ideas appeared completely foreign. After all, PLINY had stated that the combustible sulphur contained the element of fire. Belief in the infallibility and authority of the ancients was frequently so firmly established, even in the 18th century, that building on them and persistence in their notions continued instead of an independent search for fundamentally new and original ideas.

The roots of the Phlogiston Theory are touched when it is recognized that it already existed in the intellectual world of the ancients, as well as that of the Middle Ages and early modern times resulting therefrom. The primitive ideas were trying already in the time of PLINY, as we shall see, to understand the material world in terms of a number of properties, in fundamental contrast to our present way of looking at things. These properties were supposed to exist in things rather like the nymph in the well, the fairy in the flower, or the soul in the body. They were by no means always thought of as substantial in the way that the later phlogistians regarded phlogiston, but rather, in the absence of a closer scientific definition, as purely abstract. The properties in the substance were added up like, by way of example, the flavours of the ingredients in a dish — sweet, sour, salt, spicy. To avoid

losing sight of land, a few fundamental properties were assumed and supposed to be mixed in varying proportions in different substances. This intermingling of properties meant something very different from what we now understand by the compounding of a substance from its elements. Indeed, certain properties of substances were formerly symbolized by the names of elements. EMPEDOCLES' elements, fire, water, air and earth, embodied, according to ARISTOTLE, the properties warm, fluid, cold and dry respectively (and they can also be given other interpretations). But these "elements", which had nothing in common with the present conception of an element, were not, as embodied properties, drawn on to explain material characteristics. For this they were not suitable, since, in the case of ARISTOTLE's exposition at any rate, the specifically material part by which the different substances were distinguished from one another was lost. On the contrary, they were too universal, so that an embodiment of the various forms which very many substances are able to assume was later to be seen in them (fire excepted) according to an exposition differing from that of ARISTOTLE. On the other hand, other properties, and just those which more particularly characterized the material aspects, were represented as fundamental principles in which the substances were supposed to participate. Such principles are given the clearest expression in the case of PARACELUS' concepts of sal, sulphur and mercury, which correspond to the properties saltlike and involatile, combustible and volatile, and metallic respectively. In this development of concept, some sort of personification of properties by specific substances was made. BECHER, the teacher and forerunner of STAHL, replaced the principles of PARACELUS by three types of earths: vitrifying, combustible, and mercurial. Of these, the combustible earth, or *terra pinguis*, vanishes on combustion. According to STAHL it has become phlogiston. In contrast to BECHER, STAHL, in his theory, limited himself to this one property. He was thus less universal than BECHER, but instead went further in following up his ideas. By advancing the principles of translating his theory into terms of chemical reactions, he was able to formulate them in a fruitful manner, an achievement which remained denied to BECHER.

If the Phlogiston Theory is traced back to its origin, it is understandable why BOYLE's correct definition of an element was not in his day able to promote knowledge, and why, in this respect, the Phlogiston Theory was unable to apply a lever, in spite of the fact that the principle behind its application, viewed fundamentally, was not completely misleading. Labouring from of old under the prejudice that substances are composed of a few distinct properties, it was believed that certain of these, as for example the combustibility, could be extracted. It was not clear that all that which we describe by the properties of a substance constitute that substance, and that no single property as such can be wholly or partly imagined away. There was just as little clarity concerning whether a property by itself was tangible matter or not.

As long as the peculiarities of a substance were considered as given by a combination of a few principles of property, its mass was of no interest, for the properties of a substance, by which the latter is described, remain the same and are unaffected by the quantity present. The extraordinary indifference of the phlogistians towards observations of the proportions by weight in chemical reactions, which we now consider of primary importance, was thereby brought about.

Throughout the whole phlogistian age, investigators thus found themselves on a path which could not possibly lead to the discovery of the true material elements. Moreover, the Phlogiston Theory specifically led away from the aims indicated by BOYLE, since on combustion the substance burnt loses nothing material but, on the contrary, absorbs something material. In the light of the Phlogiston Theory, just those substances which we now know to be elements appeared as complex, inasmuch as they, being combustible, were supposed to contain phlogiston; while the oxides (metal calces), robbed of the phlogiston, appeared as the substances of simpler composition.

Again, briefly expressed, the abstract foundations of the Phlogiston Theory represent a combination of two conceptions. The first, already developed before STAHL's time, implied that the properties of a substance could be represented by superposition of a few fundamental properties or principles, of which combustibility, which stood at the forefront of the Phlogiston Theory, was one. The second, newly added by STAHL, consisted in the reversible transferability of this single principle, phlogiston.

After LAVOISIER's investigations of the relative proportions by weight — often recommended before him but only rarely ^{7a} properly tackled — had been carried out by means of material changes and a correct interpretation put on them, not only had the Phlogiston Theory to be given up and the oxygen theory adopted, but the mode of chemical thinking relearned from the beginning. The evidence produced by LAVOISIER from his own observations and those of others, including the important quantitative observations of JOSEPH BLACK in the year 1755 concerning the loss in weight of limestone and magnesite on roasting and the simultaneous formation of carbon dioxide (fixed air), spoke unambiguously against the Phlogiston Theory and for LAVOISIER's oxygen theory, and need not be specified here. It is not so easy to appreciate this change in the mode of thinking today. Consequently, only after a thorough analysis of the old and new modes of thought can a correct picture be made of the difficulties which had thereby to be surmounted. At first it appears to us as if the Phlogiston Theory could have been simply remodelled with the retention of STAHL's principle of transferability. Instead of saying: *Phlogiston is given up*, it was only necessary to say: *Oxygen is absorbed*, and conversely, when all was put in order. There were two reasons which made this change more difficult. The one is plain because it could be asserted directly from the experimenter's

^{7a} That is, by M. W. LOMONOSOV (see p. 17) and J. BLACK (see this page).

viewpoint. To the mind of the experimenter studying the visual phenomena and not the less obvious proportions by weight, the evolution of light and heat during combustion verified to all appearances that something is evolved on combustion. Thus, in this respect, the assertion of the Phlogiston Theory could not be completely incorrect. We recognize this objection completely today. Indeed, in one point, LAVOISIER's oxygen theory of combustion in its original form was incomplete and unsatisfying. It did not include an account of the *energy relationships*, which in the utilization of combustion phenomena for the production of heat and light are so important for mankind, more important even than the material changes which occur. We need now only to replace phlogiston by energy in order to do justice to observation. The oxidation of combustible substances liberates energy; the reduction of non-combustible oxidized substances requires the expenditure of energy.

However, at this point it would be mistaken simply to identify STAHL's phlogiston with energy, and to maintain that by the one the phlogistians really meant the other. By their phlogiston, which appeared to them as a personified property, they thought to understand something quite different. That follows, as already explained, from the roots of their theory. It was precisely because something so different was meant by the term that the relinquishing of the Phlogiston Theory necessitated a relearning from the beginning. And here lies the second reason, a considerably deeper one, felt rather than voiced at any time, which even almost a quarter of a century after LAVOISIER's discoveries caused several investigators to hold fast to the Phlogiston Theory. On recognizing the oxygen theory of combustion, one would have been obliged to give up, along with the Phlogiston Theory, the approximately 2000-year-old conception according to which the properties of substances could be derived from a few basic properties. This meant *a renunciation of the conception of the properties of substances in terms of their composition*. For LAVOISIER's oxygen theory and the concepts of element and compound resulting from it led immediately to an exactly contrary viewpoint, namely, that the properties of the elements are not to be found again in their compounds. With this new viewpoint dealing with accurately weighed materials, the changes in properties through chemical processes, that is, precisely the striking factor, remained problematical. And not only that, but it contained within itself not the smallest beginnings of an answer to the question. While this was admittedly in no way solved by the old way of thinking, it was at least represented as a problem. There was in the new material way of thinking, which resulted from the oxygen theory of combustion, absolutely no talk of connections between the properties of the reacting substances and the compounds formed from them: properties were accepted as given by experience. Thus it appeared for future investigation as if, in suppressing the quest after the properties and their connections, matter had been robbed of just its most individual character,

its properties. It was as if, to use STAHL's terminology, the leading principle, the *anima*, or, in other words, the soul, had been taken from the body. Something secret, enigmatical, and hence for the human mind alluring to perpetual contemplation, even, it could be said, something not less than mystical was banished along with the problem of change in properties from science. The overthrow of the Phlogiston Theory meant for chemical research a step which physical research had taken about a hundred years previously. It meant the overthrow of a medieval way of thinking bound up with mystical conceptions and working with shadowy definitions of ideas, in favour of a scientific investigation, which, by experiment, strove critically to prove the usefulness of the ideas and conceptions it applied to hypotheses and theories.

Modern chemical research since LAVOISIER is distinguished fundamentally from the older, therefore, in its theoretical — not experimental — attitude ⁸.

The transformation in the scientific mode of thought which occurred around 1775 was at the same time bound up with a change in the problematical element. The clinging of many investigators to the old ideas, as we have seen, was governed not only by their having to learn a new way of thinking, but was also partly based on the fact that they would thereby have had to relinquish an old problem, namely one which they were more readily able to feel than express clearly. But because this question of the cause of the change in material properties with chemical reaction could not at the time be clearly sorted out, it was also not ripe for an experimental or even theoretical treatment. Even if at first it was completely ignored by the chemistry of LAVOISIER, it had not, however, become completely meaningless. More than a century was to pass before it again forced its way forward with the development of knowledge. Today we can see clearly in which direction the new way of thinking in chemistry needed supplementing, and can express clearly the real problem which the age before LAVOISIER, with a mode of thought unsuited to scientific research, set out to solve.

In order finally to obtain an understanding for what investigators of earlier times with their personified properties actually if unconsciously had before their minds, it will suffice to glance briefly at DALTON's atomic theory, which presents a line of development following directly from the thought processes of LAVOISIER.

⁸ In his *Entwicklungsgeschichte der Chemie*, LADENBURG sees in this difference a shaking off of the shackles which had been laid on scientific investigation for almost 2000 years by the mode of thinking of the Greek philosophers. In this, however, the position is still not adequately characterized. For the Phlogiston Theory, in its origins, is to be traced back even to antiquity. (PLINY, who may well have been the first to speak of the *fire-matter* in sulphur, was in no other sense a Greek philosopher.) Nevertheless, the Phlogiston Theory with its peculiar viewpoint stood essentially in the medieval world of conceptions. Thus its overthrow meant for the transformation in the spirit of scientific investigation considerably more than LADENBURG assumes.

DALTON's atomic theory doubtlessly represents a climax in the development of the new way of thinking with concrete images instead of with scarcely intelligible abstract definitions. By it, the invisible proportions by weight, which do not force themselves directly on the senses of the lay investigator, are explained with unusual clarity. But it likewise takes not the slightest account of changes in properties when substances react, at least, not in the primitive form in which it was long used. The same is just as true of the language of chemical formulae developed from it. This shortcoming of the DALTON atomic theory was perceived by its philosophical opponents, such as, for example, SCHOPENHAUER⁹; but because of their inadequate scientific schooling they were unable to expose it clearly and significantly. In consequence, their attacks on the atomic theory, which proved itself of such valuable aid in the hands of the chemists, were never once heeded in scientific circles. But let it be considered for a moment what primitive and multifarious operations were carried out with atoms. The atoms were placed together like children's bricks, without being able to state why they continued to adhere to one another or why the properties of the elements were not visibly rediscoverable in their compounds. Only the electrochemical theory of BERZELIUS, which was subsequently to be abandoned again, represented a preliminary attempt to close this gap in DALTON's presentation. Even in the case of the elements, as certain examples show, a comprehension of the properties caused fundamental difficulties by reason of DALTON's atomic theory. How natural it was to the clear-thinking mind to identify the properties of the atoms of an element with the properties of a macroscopic tangible piece of the same, thus obtaining the latter from the former by simple summation according to the additive principle, and to say, for example: *An atom of sulphur is yellow, an atom of copper is red.* But the single example of carbon shows that this does not come off. The proof supplied by LAVOISIER that similar amounts of diamond and graphite on combustion yield the same quantities of carbon dioxide appears especially important at this point. The real "chemical puzzle", the change in properties with chemical processes, indeed, even the properties of the basic substances themselves, are not brought one step nearer comprehension by the atomic conception.

Yet this building with bricks, that is, atoms, has enormously furthered the advance in chemical knowledge, especially since critically regulated experiment was always applying a natural break to the urge to toy with arbitrarily conceived mechanical models. Even today we play successfully with such bricks which now include not only atoms but also ions of definite size, conceived essentially as spheres of fixed radii. But in so doing, one finds oneself all the more compelled to make restrictions, since the models

⁹ Cf. A. MITTASCH, *Schopenhauer und die Chemie* (Universitätsverlag C. Winter, Heidelberg).

constructed from spheres with fixed radii are not always to be brought immediately into accord with the physical properties of the substances which these models are supposed to represent. There are stipulations to be added to the simple structural principle of arranging one against the next, these being first rather vaguely indicated as being due to deformation of the structural units. In the last resort such a deformation means nothing other than a consideration of the way the bricks are linked. The joining together of atoms or ions according to some fixed structural principle does not by itself determine the peculiarities or *properties* of a substance, the *state of bonding* having also to be considered. Only then can an understanding of the properties of a substance be achieved.

That, however, is precisely the problem which, rather vaguely it is true, existed for chemistry before LAVOISIER's day, and which we now include briefly in the words *constitution* and *properties*. Its solution makes intelligible the change in properties which occur with the interconversion of substances in chemical reactions. A rigorous treatment of the problem was at that time impossible, not only because it was not clearly grasped, but also because it was inappropriately stated. That is, not only were questions asked about the *physical* properties, which depend alone upon the substance itself, but such were also interspersed with questions about an important *chemical* property, namely the combustibility. Chemical properties, however, are not based on one substance alone, but require a reaction partner. Consequently, the problem of the combustibility of a substance is not to be solved from a knowledge of its atoms and their combining ratios alone, a further knowledge regarding the vulnerability of the substance towards oxygen being required. The Phlogiston Theory picked out in an unfortunate manner — but because of its great practical significance also in an understandable manner — from the universal array of problems in the minds of PARACELUS and BECHER the one problem for the solving of which quite different and, to the contemporary way of thinking, especially remote methods needed to be adopted. Since this demanded an interpretation of the physical properties, the period around 1700 was ripe for the solving of neither the one problem nor the other.

The problem, which appeared as universal to PARACELUS and BECHER when advancing their personified properties, has become open to attack only in the most recent times. Its solution does not for a moment appear so very different from that which these investigators imagined. Its principles embody the different types of bonding which, in addition to the structural principle, determine the properties of the substance. When we talk of *heteropolar*, *homopolar* and *metallic* bonding, we mean by this essentially the same as that which PARACELUS wished to express by his types *sal*, *sulphur* and *mercury*. And if BECHER put forward essentially the same types, except that *sal* was replaced by the vitrifiable earths, then by the latter he unconsciously stated that involatile substances need not always conform to

the salt type, but can also belong to the glasses and crystalline silicates, which are not strictly heteropolar in structure. In addition, the simultaneous existence of several principles of property is possible, on the one hand because there are transitions between the individual types of linkage, and on the other because several types of linkages can occur side by side in one substance.

The fear of the phlogistians, that with the rejection by LAVOISIER and his school of the phlogistic — and thereby quite generally the older — way of thinking an essential problem of the material world would be pushed aside, thus originated from a correct feeling. They were right in believing that there were objectives to which LAVOISIER's theory could not lead. But for the development of chemical knowledge it was nevertheless important that this indefinite suspicion was not heeded further at the time, and that the rationalistic way, in supporting its theories by experiment along controlled lines of research, fairly rapidly became universal. By means of the latter, when the time became ripe for it, a quite voluntary return to the chemical enigma concerning changes in property was made. Today we see clearly where then was only dimly suspected. For all that, Nature has still enough mysteries to offer us. But, once we recognize that the time is not ripe to lift the veil, we no longer waste time and energy with speculations as in former times, but press forward along such tracks as can be laid down with the help of experiment.

3. Stoichiometry. The Concept of a Pure Substance.

The Law of Constant and Multiple Proportions

The overthrow of the Phlogiston Theory did not merely mean the introduction to chemistry of the new mode of thought that brought the concept of *composition of matter* into a new light. The quantitative principle by which LAVOISIER investigated these relationships meant a simultaneous application of the art, already long employed in physics, of *exact measurement*. This permitted the translation of chemical observations into numerical terms. To be sure, the measurements were limited to the method indicated by LAVOISIER for determining the quantitative relations between the reacting substances and their reaction products. Chemistry was thereby for the first time linked to mathematics, which had already long been the case for its sister science, physics. This common linkage brought nearer the two branches of knowledge, which until then had had but little contact with each other. From that point onwards, physical thinking gradually made itself at home in chemistry. The necessity of approaching chemical problems by the thought-media of physics and mathematics was admittedly recognized before LAVOISIER's time. Concerning this, the clearest and most

detailed utterance is possibly due to M. W. LOMONOSOV¹⁰. He remarked also that in chemistry there are measurable properties, which, as he put it, evoke a clear picture, and those whose measurement appears to be impossible, at least directly, such as colour, smell, cohesion. (Of the latter, also, some have become measurable through progress in knowledge.) LOMONOSOV recognized the significance of weighing as a measure of mass, and, in 1756, 18 years before LAVOISIER, proved the Law of Conservation of Mass for chemical processes by oxidizing metals such as tin and lead in closed vessels¹¹. But he in no way limited himself to mass, and in his physicochemical investigations of salts gives a full programme of measurable properties and changes in properties with chemical processes such as solubility, density, changes in volume and temperature on dissolution, boiling point, rate of solution, optical refraction and capillarity, of which he himself tackled only quite a small part. Physical chemistry first executed this programme about 100 years later.

In this, however, as in the measurement of the quantitative proportions of matter in chemical reactions, which at first was undertaken almost exclusively, the application of mathematics to chemistry was of a different — one might say more primitive — kind than its application to physics. Certainly, in the former case as well as in the latter, there were measurements; but whereas in physics it was very easy to bring these into relatively simple functional relationships with each other, this did not at first succeed in chemistry. Thus the equivalent and atomic weights of the elements remained numbers between which no clearly recognizable functional relationship arose, as did the solubilities, boiling points, and so on. Only the development of thermodynamics made it possible to relate some at least of the thermodynamical quantities. It was this line of development in physical chemistry which attacked the problem of chemical affinity by a mathematical treatment. It could not have afforded to forgo a physicomathematical schooling. For LAVOISIER's methods, on the other hand, in which attention was directed to the masses of the reacting substances, no previous mathematical training beyond that in the four fundamental types of reckoning was necessary. The whole of stoichiometry and language of chemical formulae were able to develop on these simple foundations. The equations set out by their help meant a form of expression to chemistry similar to that which mathematical equations meant to physics, but demanded, in contrast to most of the latter, no especial mathematical understanding. Yet, in the experimental derivation and theoretical establishing of the stoichiometric Laws of Constant and

¹⁰ M. W. LOMONOSOV, *Tentamen Chymiae physicae in usum studiosae juventutis adornatum* (1752); *Dromus ad veram Chymiam Physicam*. OSTWALD's *Klassiker der exakten Wissenschaften*, Vol. 178, p. 39. B. N. MENSCHUTKIN, *M. W. Lomonossov as a physical chemist. A contribution to the history of chemistry in Russia* (Petersburg, 1904, in Russian).

¹¹ In this he also recognized the cause of the erroneous conclusion of BOYLE for a similar experiment in the year 1673. BOYLE ascertained an increase in weight because he reopened the vessel after the experiment and allowed the air to enter.

Multiple Proportions, not unimportant intellectual difficulties of a non-mathematical nature arose, of which one is able to gain a clear vision today.

The Law of Constant and Multiple Proportions. — The universal basis of this law is the Law of Conservation of Mass for chemical processes, discovered in 1785 by LAVOISIER and finally proved in 1908 by LANDOLT and 1909 by EÖRVÖS¹².

The Law of Constant Proportions rests on two established points which are quite independent of each other.

(i) If two substances react with one another to form one or more discrete new substances, then they do this in a quite definite ratio. Reverting to the elements, this fact can be expressed: In a particular compound the elements are combined with one another in a fixed, unchangeable, quantitative ratio. Or: The proportion according to which a compound is composed from its elements is constant.

(ii) For any compound of two elements the proportion by weight is again encountered in other compounds containing the same elements.

In order to make it universally valid, this Law of Constant Proportions requires supplementing by the Law of Multiple Proportions. According to this law, not only is a single ratio possible, but several ratio values which themselves are in the ratio of small whole numbers.

The Law of Constant and Multiple Proportions can be expressed in a combined form. Of the different forms it can take, one runs:

If substances react together, they do so in a fixed ratio or several fixed ratios which in turn bear simple integral ratios to one another.

Again reverting to the elements, it can here be said: The elements each possess a relative number, the *combining weight*, which fixes the quantitative proportions in which the elements enter into combination. When the elements combine to form compounds, they do this in the ratio of their combining weights or integral multiples thereof.

The Law of Constant and Multiple Proportions therefore asserts two things:

(i) The composition of any particular compound is constant.

(ii) The composition of different compounds are not independent of one another, but the proportions by weight of the component elements are governed by fixed numerical ratios and integral multiples of them.

The former statement in the last resort is nothing other than a *definition of the concept of a chemical compound*, or, alternatively, of the *concept of a pure substance*. As already mentioned (p. 3), LAVOISIER and many chemists with him assumed the constancy in composition of pure substances

¹² That, according to the modern theoretical viewpoint, changes in mass occur lying far outside the limits of detection by the methods of quantitative chemical analysis, and whose dimensions are determined by the change in energy which takes place simultaneously, is a point which need not be considered here, although for the sake of completeness it must receive mention. In processes bound up with quite a different order of energy change from that occurring in chemical reactions, these changes in mass cannot be neglected (see p. 291).

as almost a matter of course. For several salts this assumption had since 1772 been proved correct by the analyses of C. F. WENZEL. The definition of the concept of a pure substance based on these was first proved to be quite generally applicable by reason of the experience collected in the period 1801—1807 during the controversy between PROUST and BERTHOLLET. PROUST defended the constancy in proportions, while BERTHOLLET denied it or allowed its validity only in a few cases. Numerous substances, as for example common salt, mercuric oxide, water, carbon dioxide, irrespectively of the manner of preparation, always exhibited the same composition on quantitative analysis. Analysis has to be preceded by a purification of the substance and an examination of its purity¹⁸. From the viewpoint of the analyst, a substance can be regarded as pure if its properties do not change by any measurable amount during various purifying operations; two substances pass as identical if they agree in their properties. The precision with which such an agreement can be ascertained, like the verification that the properties do not change on further purification, depends on the sensitivity of our means of measurement. Effecting a purification depends moreover on the chemical as well as the physical aids to the "art" of separation. We possess now, however, a vastly more accurate method for ascertaining the degree of purity of a substance than differences in quantitative analyses permit. By way of example, the analysis by weight of a sample of sodium chloride, which spectroscopically exhibits the presence of 0.01 % of potassium chloride, gives the same results as a spectroscopically pure sample.

With substances which can be melted, volatilized or recrystallized unchanged, purification and tests for purity encounter no fundamental difficulties. Often enough a sharp melting point, boiling point or sublimation point serve as a criterion of purity, as, for example, for water or carbon dioxide. But the very attempt to determine the degree of purity of mercuric oxide by physical methods will bring one into difficulties, and likewise the attempt to purify this substance. All that can be done is to wash it with solvents which leave it unchanged, thereby freeing it from substances soluble in these solvents. In place of the physical tests, there is the test of chemical analysis in which it is postulated that the composition of a substance is an unchangeable property belonging to it. Since the composition of a substance is regarded as something just as specific as the other properties expressing the nature of the substances in daily life and in science, the constancy in quantitative content of its elements provides a *definition* of a pure substance.

This definition is eminently suitable, as has been taught by the development of chemical knowledge, but is in no sense essential. In daily life the idea of a substance includes substances known under collective terms, which vary between limits in their composition as well as in other properties,

¹⁸ Deficient purity of the substances analyzed led BERTHOLLET to the erroneous experimental results which he used in open support of his views. PROUST, in contrast, tried if possible to convince himself before analysis that he was not dealing with a mixture.

as, for example, brass or glass. Not only in daily life but in science also it is on occasions necessary when dealing with a pure substance in the scientific sense according to the foregoing definition, to allow a certain latitude in the values of individual properties far exceeding the uncertainties in measurement. By way of example, pure copper has a rather different density and a somewhat different conductivity according to whether it is cast, hammered or rolled. From the general viewpoint of science, it therefore appears on occasions completely permissible, with respect to the idea of a pure substance, to allow also a certain variational latitude in the composition overstepping the precision of the analytical methods. Nevertheless, such cases are more appropriately treated as exceptional. In order to gain a broad appreciation of the essential features of the laws governing the composition of substances, these may *initially* be put on one side.

The law of constant composition behind the usual definition of a pure substance is however by no means identical with the Law of Constant Proportions. The latter is also no logical consequence of it, but is something quite new and given by experience. For it is in no sense self-evident that, for example, lead and sulphur are contained in the same quantitative ratio in lead sulphide and lead sulphate. This law was derived as an experimental fact, firstly by investigations on a limited number of substances. In 1792, J. B. RICHTER utilized the fact then already known and which he once again accurately checked, namely that the solutions of two neutral salts such as sodium nitrate and potassium chloride remain neutral on mixing, and came to the important conclusion that on neutralization different bases correspond in constant quantitative ratio to different acids, and hence that conversely there must be equivalent weights for individual acids and bases. Thus, by way of example, if nitric acid when compared with hydrochloric acid required relatively more caustic potash than caustic soda, then the solution formed on mixing similar quantities of sodium nitrate and potassium chloride, in the event of double decomposition taking place — that is, by the precipitation of saltpetre — would become acid, since the quantity of potassium contained in the potassium chloride would not suffice to neutralize the nitric acid contained in the sodium nitrate.

The equivalent weights themselves cannot be deduced solely from the observation that the solution remains neutral. Special experiments must be carried out for their determination. By virtue of such experiments, RICHTER, in 1798, published tables which contained equivalent weights (then not so named¹⁴). From these, E. G. FISCHER¹⁵ was later to compile the first table of equivalent weights.

In spite of RICHTER's logical manner of reasoning in the derivation of the Law of Constant Proportions, and of the precision of experimental

¹⁴ The expression *equivalent* was used for the first time by WOLLASTON in 1814. Cf. in this respect pp. 24, 25.

¹⁵ In his translation of C. L. BERTHOLLET's *Essai de Statique Chimique* (1811).

data, RICHTER's results remained without influence on the development of knowledge. Their significance was first rightly appreciated some time later by BERZELIUS. The latter, it is true, made the mistake of attributing a part of RICHTER's work to C. F. WENZEL¹⁶, in particular his interpretation of the neutrality rule, so that it was only much later, not least by the efforts of W. OSTWALD¹⁷, that RICHTER's services to the scientific world became fully acknowledged¹⁸. One reason for the poor response which RICHTER's labours at first awakened is to be sought in the fact that, by its nature, the hypothesis-free derivation of the Law of Constant Proportions from the neutrality law lacked clarity and demanded a logical kind of thinking unusual in his day. A second reason lies in RICHTER's out-of-the-way experiments, in his seeing cryptic algebraic relationships in the values obtained by him for the equivalents of acids and bases, and in his practising with them a kind of numerical mysticism, in addition to his obscure mode of expression in numerous — though not in decisive — places in his works. Finally RICHTER did not arrive at his results by the direct route. Although he coined the expression *stoichiometry*, he did not really set out with the view of investigating the composition of substances. Rather he wished to measure the chemical affinity between acids and bases, and believed he had found a measure of them in the *quantities* by which they neutralize each other. His achievement is that he measured something exactly, namely the quantities of material, and that he understood how to combine correctly the results thereby obtained with the law of neutralization. In failing to achieve his own aim of measuring affinity, he discovered a law completely independent of it.

In this manner, a variety of circumstances had collectively worked by means of a plain hypothesis, the *atomic theory* of DALTON, to bring the meaning of the Law of Constant and Multiple Proportions before the eyes of the scientific world and invite an experimental proof which was then to be executed principally by BERZELIUS.

The experimental starting-point of DALTON was not constant but *multiple* proportions. He found in several instances that two elements could combine not in one ratio only, but in several ratios, the values found for these being in the ratio of small whole numbers. In order to explain this fact he drew on the concept that matter was constructed of the minutest of particles. This, being in its origin a purely speculative utterance of Greek philosophers, demanded as speculation the same justification as the continuum theory of matter supported by other philosophers. The concept of the construction of matter from the minutest of particles had already received various applications in science as a straightforward aid to the qualitative explanation of phenomena, as in the attempt to understand the occurrence of sub-

¹⁶ WENZEL had merely produced material in proof of the constancy in composition of substances (p. 3, footnote 4).

¹⁷ Further also by C. LÖWIG, *J. B. Richter, der Entdecker der chemischen Proportionen* (memorial review, Breslau, 1874.)

¹⁸ A. LADENBURG, *Entwicklungsgeschichte der Chemie*, p. 53 (4th Ed., 1907).

stances in various states of aggregation, and in the first beginnings of a kinetic theory of gases by BERNOULLI in 1738. Quite independently of these earlier spheres of application of the atomistic hypothesis, DALTON now applied the atomic theory in order to obtain an understanding of multiple proportions, whence constant proportions, which finally are only a special case of multiple proportions, also follow at the same time from his theory. DALTON assumed that the atoms of an element were all equally heavy and that, whenever a chemical compound was formed, only a small number of atoms combined with one another. He regarded 1 : 1, 1 : 2 and 1 : 3 as possible multiples, these being derived partly from his experiments, and partly also from unproved assumptions. The ratio 2 : 3 received no mention, and he appears to have held it as inadmissible.

DALTON's explanation is so eminently lucid that it promotes nothing less than fascination. In the last resort it was this fascinating effect which caused BERZELIUS to undertake a proof of the Law of Constant and Multiple Proportions on the broadest basis. BERZELIUS recognized, however, that this law was not *necessarily* a consequence of the atomic theory, for the latter contained no sort of limitation concerning the multiples in which the atoms of the elements could take part in the formation of a compound, and also in particular did not imply that the multiples should always correspond to small whole numbers.

BERZELIUS consequently set himself the task of first determining the multiples by experiment, and then linking them with the atomic theory. As far as the first part of the task was concerned, he accomplished this with an analytical precision unknown until that time, thereby ascertaining that a very large number of substances possessed a constant composition¹⁹. With this, the PROUST-BERTHOLLET conflict appeared as finally settled in favour of the former. Likewise the Law of Constant and Multiple Proportions was shown, with the highest analytical accuracy attainable, to maintain its validity for inorganic compounds. Among the multiples encountered were none higher than 7²⁰. On the other hand, organic compounds supplied him with various multiples which were no longer quite such small numbers. BERZELIUS therefore at first called in question the validity of the Law of Multiple Proportions for organic compounds²¹, but yet later accepted its universal validity²². The question why, in the case of organic compounds, the multiples were frequently not *small* whole numbers he left open. In general, he satisfied

¹⁹ How conscientiously BERZELIUS set about this is shown by his instructions for the utilization of quantitative analyses. The result of a single analysis must never be relied upon, it being essential that the result be derived from an agreement between analyses carried out on the same substance prepared by at least three different methods and analyzed by at least two different analytical procedures.

²⁰ For binary organic compounds this limit is still valid today, with the solitary exception of OsF₆.

²¹ *Essai sur la Théorie des Proportions Chimiques et sur l'Influence de l'Electricité*, p. 26 (1819).

²² *Lehrbuch der Chemie* III, 1, p. 141 (1827).

himself for the case of inorganic compounds essentially by establishing integral multiples, only casually touching the question why they were always small numbers. In this he pointed to the geometrical fact that a sphere could be touched by at most twelve others of similar size ²³.

The second part of the task, the connecting of the multiples with the atomic theory, had already been attempted by DALTON, who, however, had set to work along most arbitrary lines. But in the establishing of a fixed, simple, numerical ratio of atoms for individual compounds, he obtained the possibility of relating the experimentally found proportions by weight with the weight ratios of the atoms of the component elements, and of formulating a *table of atomic weights*. BERZELIUS tried to avoid the arbitrary assumption of DALTON in determining the multiples, in that he tried to replace it by something better-founded. Quantitative analysis cannot supply this, since only numerical ratios follow from it. These, in different compounds of the same elements, exist in the ratios of small whole numbers to each other, but do not give the numbers of the atoms themselves, since it is not known which of the various multiples found corresponds to one atom. BERZELIUS therefore linked the Law of Multiple Proportions with the law of gaseous volumes newly discovered by GAY-LUSSAC, according to which the volumes of gases undergoing chemical reactions are in the ratio of small whole numbers. For the elements, he equated the relative number of volumes with the relative number of atoms, assuming in water, for instance, two atoms of hydrogen to one atom of oxygen, since two volumes of hydrogen unite with one volume of oxygen in the formation of water. In numerous other cases in which the elements do not react as gases, this kind of inference cannot be made. Thus BERZELIUS was obliged, not unlike DALTON, to allow a certain arbitrariness to hold sway over the drawing up of his atomic-weight tables. Nevertheless, he was here governed by a more reliable instinct than DALTON, and was subsequently able to utilize certain analogies in the compounds of different elements, more particularly isomorphism, in order to fix the atomic weights. In this he formulated compounds behaving similarly with the same relative numbers of atoms.

That which RICHTER achieved for acids and bases in his construction of a *table of equivalent weights* was now realized for elements by DALTON and BERZELIUS in the setting up of a *table of atomic weights*, but with one difference in the experimental evidence. The equivalent weights of RICHTER were unequivocal, since the neutralization of acids and bases could be effected only in a single ratio governed, of course, by the Law of Constant Proportions alone. For elements, on the other hand, it was frequently not possible to give an unchangeable equivalent weight, since in their compounds the Law of Constant Proportions is joined by that of Multiple Proportions. For an element, therefore, analytical results frequently supplied several equivalent

²³ *Lehrbuch der Chemie* III, 1, p. 36.

weights related in the ratio of small whole numbers. Consequently the idea of equivalence was here ambiguous. This ambiguity was avoided in the case of atomic weights. With these an uncertainty had to be taken into the bargain since the relative number of atoms in the compounds could not be determined with certainty. It was only natural to *combine the table of atomic weights with that of equivalent weights*. But as long as the relationship of atomic weight to equivalent weight or, where appropriate, to the varying equivalent weight remained undetermined for each element in its respective compounds, it was not possible to link both together in an *unambiguous* manner. It was therefore a serious blunder when WOLLASTON, who in 1814 first used the term equivalent, undertook this combination simply by identifying *equivalent* according to RICHTER with *atomic* according to DALTON; for it was already certain that the ratio atomic weight : equivalent weight was not the same for all elements, since for numerous elements there were various equivalents, while there could be only one atomic weight. One could only hope to comprehend firmly the said ratio atomic weight : equivalent weight, expressible by a whole number, on succeeding in removing the arbitrariness in choice of atomic weights still extant with BERZELIUS.

The most significant advance in this direction was achieved when the theoretical import of the law of volumes for gases, which had already been employed by BERZELIUS, was correctly recognized. The state of affairs was less simple than BERZELIUS had assumed. It sufficed, namely, to clarify the question of the ratio in which the smallest particles of the gases stood to the smallest particles assumed for matter by DALTON; or, in other words, to determine whether the physical division of the elements on passing to the gaseous state was as complete as the chemical on entering into chemical combination. The way had already been indicated in 1811 by AVOGADRO's Hypothesis, according to which, under similar conditions, a fixed volume of any gas contains the same number of smallest particles. In order to be able to recognize whether or not these were atoms in the case of gaseous elements, not only was a consideration necessary of the ratios between the volumes of the gaseous elements, but also between the gaseous *compounds* of gaseous elements. BERZELIUS had left this out of consideration. The combination of the physical concept *molecule* according to AVOGADRO and the chemical concept *atom* according to DALTON supplied the scientific world with such difficulties in thought, however, that it was only about fifty years later that its eyes were opened by S. CANNIZZARO; and this notwithstanding that the correct beginnings were to be found with AVOGADRO himself, and that meanwhile in 1831, M. A. GAUDIN in a work which remained unheeded, had already given a detailed discussion of the matter.

Reference only will be made in this context to the other means of establishing the correct atomic weights, of which the law of nearly constant atomic heats of DULONG and PETIT (1818) is especially noteworthy. Further

criteria were supplied much later (1869) by the Periodic System of MENDELÉEF and LOTHAR MEYER.

After the correct atomic weights had at last been settled, the ratio atomic weight : equivalent weight could also be determined. This came to be known under several names, first saturation capacity, later atomicity, and finally *valence*. For the various elements for which only *one* equivalent weight had previously been established, it proved to be a by no means identical, but characteristically different and consequently important criterion of chemical behaviour for the respective element. It thereby becomes apparent how truly portentous the equating of atomic and equivalent by WOLLASTON was for the development of scientific knowledge.

In these valencies, which can be expressed by whole numbers, rests, in the last resort, the secret of the small integral multiples determining the numerical ratio of the atoms in a compound according to the Law of Constant and Multiple Proportions. Whether on occasions still other factors play a part in fixing the numerical ratios, such as, for instance, geometrical considerations much in the sense that BERZELIUS had indicated in his representation by spheres, is a new question which no longer solely concerns the number, but rather the *kind* of arrangement of the atoms in a compound.

The Law of Constant and Multiple Proportions is thus by no means so simply linked with the atomic theory as might have appeared after the derivation put forward by DALTON. As has already been emphasized, it was also not a necessary consequence of DALTON's atomic theory. On the other hand, the introduction of distinguishable kinds of smallest particles, namely molecules and atoms — termed *molécules intégrantes* and *molécules élémentaires* by AVOGADRO — was unavoidable when small multiples similarly provided by GAY-LUSSAC's Law of Volumes were connected with AVOGADRO's Hypothesis. Here one is led directly to the atomistic hypothesis, while DALTON, without logical deduction but with inspired intuition, introduced the atomic theory, with which he was familiar through philosophical speculation, to chemical science in order to explain the Law of Multiple Proportions discovered by him. Owing to the intuitively evident nature of DALTON's deductions, it was later overlooked that they were neither compelling nor complete; thus they have been frequently presented as if the Law of Constant and Multiple Proportions was a self-evident consequence of them.

On recognizing that DALTON's obvious method of drawing conclusions was not compelling, while the opposite was true of RICHTER's obscure method of arriving at the Law of Neutrality and Law of Equivalents, and thereby the Law of Constant Proportions, OSTWALD had thought it possible, while avoiding the atomistic idea, to derive the Law of Constant and Multiple Proportions by means of a logical train of thought of the same general type, and that too from the concept of a pure substance and its unchangeable

composition²⁴. In this he fell into a fundamental error²⁵, since, as was emphasized at the beginning, experimental support transcending the observation that pure substances possess a constant composition was necessary, even for the Law of Constant Proportions. It was because of the very nature of things that BERZELIUS in his analytical investigations, which had the proving of this law as their object, had reopened the question of the experimentally derived principle of constant composition of pure substances, and confirmed it much more rigorously than was possible for PROUST during his controversy with BERTHOLLET.

Through the comprehensive confirmation of PROUST's views, the opinion that under certain circumstances substances might exist with their elements not in stoichiometric proportions, yet for which a state of uniformity could not be denied, had fallen into oblivion. The results of the analysis of certain minerals, in particular magnetic pyrites, for example, where the numerical ratio of the atoms Fe : S is not 1 : 1, were silently passed over. From the theoretical viewpoint, however, these considerations could not be laid aside, since a theoretical confirmation of the universal validity of PROUST's views had not been supplied on the basis of the atomic theory, and indeed is not forthcoming.

4. Chemical Affinity

When it became recognized that the wide diversity in the material world was built up from only a few basic substances, it became timely to learn what possible combinations between the elements were realizable, and what the conditions of existence of the preparable compounds were. That the combining of elements to form chemical compounds did not exhaust all the possibilities imaginable, could already be gathered from the

²⁴ *Grundriss der allgemeinen Chemie*, p. 131 (5th Ed., 1917). *Lebenslinien* II, p. 373. The train of thought itself is repeated in W. OSTWALD's *Prinzipien der Chemie*, p. 385 (Akad. Verl., Leipzig, 1907). From this it follows that in the derivation of the natural law, which it is attempted to prove, the latter lay hidden from the beginning, for the derivation provides no limits to the numerical ratios which may appear as the ratio of small whole numbers.

²⁵ Likewise a similar error of thought exists in the works of F. WALD, in which he attempts to derive the fundamental stoichiometric laws without the aid of the atomic theory: *Genesis der stöchiometrischen Grundgesetze* I and II, *Z. physik. Chem.*, 1895, 18, 337 and *ibid.*, 1896, 19, 607; *Die chemischen Proportionen* I and II, *ibid.*, 1897, 22, 253 and *ibid.*, 1897, 23, 78. A critical analysis of the reasoning behind WALD's statements cannot be given here. Even if WALD did not succeed in deriving the fundamental stoichiometric laws from universal assumptions concerning the composition of phases, he nevertheless perceived clearly many things which in his day were almost invariably passed over without a thought. He is thus not completely wrong when he asserts that the chemist, in drawing up phase systems, himself puts the Law of Simple and Multiple Proportions into them (18, 338); in this, however, as set forth above, it is justifiable to deal *first* with substances as chemical compounds submitting themselves to these laws, since their number is considerable. That the study of phases of variable composition had been completely and unjustifiably neglected for a long time was likewise rightly emphasized by WALD: "Die Phasen variabler Zusammensetzung werden vom Chemiker ignoriert, die von konstanter Zusammensetzung speziell studiert" (18, 343).

current knowledge of chemical compounds. It was striking, even on casual observation, that many substances very readily enter into reaction with one another, others less readily and some not at all. Approximate knowledge of the reactivity of elements and compounds rendered an intentional preparation of certain compounds possible. First, the knowledge concerning which substances reacted with each other and which not had to be accepted as given by experiment. By gathering experience one very soon obtained a correct feeling for the direction a reaction would take in relatively simple cases, for example, that hydrochloric acid and zinc would react to form zinc chloride and hydrogen, and not zinc hydride and chlorine. For the beginner, who did not possess sufficient experience, such predicting naturally caused difficulties. Thus an immediate search was made for regularities in the experimental material, and for a representation which permitted the explanation of such regularities and the prediction of others. Out of this endeavour developed the concept of *chemical affinity*. One said that elements combining vigorously with each other possessed a high affinity for one another, like, for example, iron and sulphur, or hydrogen and oxygen; elements whose compounds easily decomposed, like, for example, mercuric oxide, possessed only a low affinity.

This concept of *chemical affinity* differs characteristically in its nature from other scientific concepts, though like the latter, it was taken from the language of daily life. But, in contrast to the others such as force, matter and current, *it did not originate in sensual perceptions*, which in the last resort always possess a physical content, but was borrowed from the *purely spiritual world*. Just as certain individuals felt drawn to one another, so did certain elements feel drawn to each other, others mutually repelled. Emotional feelings from the world of men were here utilized for the formation of a scientific concept. This "mystic"²⁶ origin of the idea of chemical affinity is very clearly expressed by the allegory which GOETHE furnishes in his "*Wahlverwandschaft*" (that is, "*electic affinity*"). By bringing chemical changes, that is, natural processes into a common plane with the human world of feeling, much confusion thereby arose, and for a time the real problem behind "chemical affinity" was veiled. The older chemical text-books suffered by having to begin with a discussion of a thoroughly obscure concept, since, owing to the significance of the reactivity of the various elements and compounds for the course of chemical reactions, they believed themselves obliged to place the concept of affinity in the forefront. Even in the case of BERZELIUS, who himself was able to take a significant step forward towards the recognition of the cause of chemical affinity, the introductory discussions about chemical affinity in his text-book are vague, and lack the exactness present later in the discussion on the quantitative proportions by weight of the elements in chemical compounds. In this manner, the beginner is first led on to shaky ground without clear directional guidance,

²⁶ C. L. BERTHOLLET, *Essai de Statique Chimique*, p. 2 (Paris, 1803).

before travelling along well-founded paths on the firm soil of more certain knowledge. This kind of introduction to science was without doubt detrimental to many investigators and sometimes may well have been the reason why the chemist did not always easily befriend himself with the exactly defined concepts of physics.

The concept of affinity, it is true, received a physical aspect when C. L. BERTHOLLET²⁷ characterized as affinity those forces acting between the smallest particles (*molécules*) and giving rise to chemical phenomena. BERTHOLLET believed that a certain order had for the first time been brought into the diversity of chemical compounds by the hypothesis of chemical affinity, and that a line of research conscious of its aim had been opened up. In point of fact this hypothesis was of no assistance either before or after BERTHOLLET. The researches into the proportions by weight by means of chemical reactions could have been just as conscious of purpose without the existence of the concept of affinity, and were partly accomplished without any reference to it.

Absolutely nothing was in reality gained by BERTHOLLET's definition, it being merely the substitution of one word in the place of another. The physical trimmings served solely to veil the hollowness of the concept. The statement that where ideas fail words are never lacking applies with particular aptitude here. Forces were put forward as the cause of affinity analogous to mechanical attraction, without in any way indicating the possibility that they were to be related with other natural phenomena. Indeed, this notion of forces led to a conception which hindered later development. The force of affinity was supposed to exhibit itself between dissimilar particles as, for example, the reaction between acid and base teaches. The force between similar particles was distinguished from it as cohesive force. This differentiation was advanced at the same time to meet the anthropomorphic origin of the expression affinity. Frequently individuals with different dispositions and temperaments feel drawn towards one another. Unfortunately the first true recognition of the nature of chemical "forces" so aided and abetted this representation, that to all appearances it became raised almost to the level of a dogma (see later).

This first cognizance of the nature of chemical "forces" was obtained by BERZELIUS from the chemical action of the electric current. The same polarity which was apparent in electrical phenomena was also, so it was thought, present in the atoms, driving them into combination with each other. For this reason, BERZELIUS tried in 1818 to arrange the elements in a sequence according to their electrical behaviour, beginning with the most electronegative element, oxygen, and ending with the most electropositive element, potassium. In this he trod a completely new path. Attempts of a similar kind, but embracing a much more modest number of elements, were embodied in the otherwise completely heterogeneous affinity tables of the 18th

²⁷ *Essai de Statique Chimique*, p. 24 (1803).

century. In the last resort they originated in the order of precipitation of certain metals worked out by ANGELUS SALA in the year 1617, who thereby expressed observations concerning the ease of precipitation of a metal from its salts by another: Au—Hg; Ag—Cu; Au—Ag; Cu—Fe. Since then, attention was constantly being drawn to this series, which was meanwhile extended. In 1683, STAHL found a parallel in the rates of solution of the metals in acids: Zn, Fe, Cu, Pb (Sn), Hg, Ag, Au. WENZEL drew up a series practically identical with that of STAHL in the affinity of metals towards acids: Fe, Pb, Sn, Cu, Sb, Hg, Au: and towards sulphur: Fe, Cu, Sn, Pb, Ag, Sb, Hg. In 1798, J. W. RITTER recognized the parallel between the electromotive series prepared meanwhile by VOLTA, the displacement series, and the tendency of the metals to combine with oxygen. BERZELIUS was able to follow on from here. It is only a small step from RITTER to the measurement of electrochemical affinity in the modern sense, which is now quantitatively possible. In the first half of the 19th century, one had admittedly to be content with the measurement of the potentials of voltaic cells constructed from various metals. This way was tragically obstructed by BERZELIUS, in that he attributed a much too general validity to his electrochemical theory, and placed elements in the series where they did not belong. That is seen by a glance at the approximate order of the elements which he gives "with respect to their general electrochemical properties and those of their stablest oxides"²⁸:

O S N Cl I F P Se As Cr Mo W B C Sb Te Ta Ti Si
 Os H Au Ir Rh Pt Ag Pd Hg Cu U Bi Sn Pb Ce Co
 Ni Fe Cd Zn Mn Zr Al Y Be Mg Ca Sr Ba Li Na K.

Although there was a correct kernel in the idea of relating the electromotive series with chemical affinity, BERZELIUS, for the reason stated, did not follow it up correctly, but renounced from the first the measurement of affinities, contenting himself with a qualitative assertion which could be simply grasped, namely, that chemical compounds must have a polar construction. The *Theory of Electrochemical Dualism* constructed on this fundamental idea was, in point of fact, able to bring a large number of chemical processes nearer to the understanding than was the purely formal, dualistic formulation of salts by LAVOISIER. This applied more particularly to the reactions of acids, bases and salts in aqueous solution, which had been especially closely studied. But although a correct nucleus existed in this first genuine theory of chemical affinity, it could only be maintained for a little over two decades. The reason for this is to be sought in two different causes. It was mostly observations on the substitution processes of organic compounds which contributed towards its relinquishment; for here elements, which according to their usual chemical behaviour exhibited the opposite polarity, like hydrogen and chlorine, were able to substitute one another and fulfil

²⁸ *Lehrbuch der Chemie* III, 1, pp. 66—67 (1827).

similar functions. The concept of an opposing polar nature of affinity forces exerted an almost stifling effect on the advancement of knowledge, inasmuch as it hindered BERZELIUS and other investigators from applying the AVOGADRO Hypothesis logically and accepting the smallest particles of gases such as hydrogen, oxygen and chlorine as constructed of two similar atoms, which would have resulted in a clarification of the two concepts, atom and molecule²⁹. But a second deeper-hidden cause was responsible. BERZELIUS had attributed larger or smaller positive and negative electrical charges to the atoms themselves, and thereby an excess of charge to the compounds formed between them. For example, $\overset{+}{\text{S}}\overset{-}{\text{O}}_3$ was supposed to be negatively and $\overset{+}{\text{K}}_2\overset{-}{\text{O}}$ positively charged, so that a combination to K_2SO_4 would result. This assumption of different degrees of charge on the elementary particles in combination stood however in contradiction to the fundamentals of the theory of electricity; for the compounds sulphur trioxide and potassium oxide are in themselves uncharged and hence could not possess an excess of the one or the other kind of electricity, such as would have arisen from the heavier charging of the negative or positive partner.

Indeed, it herewith became apparent that the physical attack by BERZELIUS must be wrong. However, it was not made clear where he actually erred. BERZELIUS confused two things, namely, the *potential* between oppositely charged condensers, which effects an electrostatic attraction, and the adjustment of charge which results on contact between the two electrically charged condensers, in which *quantities* of electricity are involved. In the last resort he was not clear about the difference between the intensity and capacity factors in electrical energy. His signs + and - consequently mean not merely quantities of electricity, but involve a vaguely felt symbolism of *striving* for + and - charge. He was not able to differentiate the latter correctly from existing charge. That BERZELIUS's error must have lain here is seen from the following consideration which prevailed over his thought processes. If the placing of an element in a "potential sequence" corresponds to a content of positive or negative charge in its atoms, as measured by the quantity of electricity, then the elements consisting of atoms must be collectively charged, which is contrary to experience. However, BERZELIUS regarded the combining of two elements to form a compound as accomplished like the adjustment of charge which results between a positively and a negatively charged condenser³⁰; if one is more heavily charged than the other, the corresponding excess of charge remains, which makes a further exchange of charge with a third, oppositely charged condenser possible. The electrical charging of a compound here assumed had, however, just as little reality as an electrostatic charging of the atoms.

For the atoms themselves, in order to explain why strongly electro-

²⁹ S. CANNIZZARO, p. 53 (memoirs in Italian).

³⁰ *Lehrbuch der Chemie* III, 1, p. 63.

negative elements like oxygen and sulphur could combine with one another, BERZELIUS made the following bold hypothesis³¹. The atoms, with the exception of the most electronegative, the oxygen atom, were supposed to possess two poles, a positive and a negative. With the electropositive elements the former "preponderated", with the electronegative the latter. Which of the two poles was active on the formation of a compound supposedly depended on the nature of the partner. Thus the strongly electronegative sulphur employed its positive pole towards the still more electronegative oxygen in the compounds SO_2 and SO_3 , but its negative pole towards the electropositive metals and hydrogen. The electrochemical opposition supposed to exist in the compounds $\overset{+}{\text{K}}_2\overset{-}{\text{O}}$ and $\overset{+}{\text{S}}\overset{-}{\text{O}}_3$, for example, was thus also postulated for the atoms, which accordingly were made into what we now call dipoles. BERZELIUS's polarity differed fundamentally from the modern concept of a dipole, in that, for atoms as well as compounds, a preponderance of one pole was assumed. If this preponderance was not meant to signify an electrostatic charging of the atoms and compounds capable of forming compounds of a higher order, BERZELIUS must actually have thereby meant a latent electrical potential corresponding to the potential governing the chemical affinity. Thus, as when in the presence of an electric potential between two condensers a spark is transmitted, so two substances on combining compensate by the evolution of light and heat³². Such a potential can naturally not be measured electrostatically in the usual way. Nevertheless, BERZELIUS operated with it additively and subtractively, as if he were dealing with quantities of electricity. He overlooked in the supposed electrical analogue that the stronger or weaker charge of a condenser, which fixes the potential difference, is not governed entirely by the quantities of electricity brought on to the condenser, but also depends upon the capacity. In the additive and subtractive treatment of the intensity factors of energy, potential difference and force, his line of thought — and also his error³³ — was closely related to the doctrine of changing affinity values for chemical compounds, where "valence forces" were also added and subtracted in a forbidden manner just as if they were masses³⁴. The physical confusion concerning the fundamentals of his electrochemical theory also prevented BERZELIUS from understanding FARADAY's Law correctly.

The significance of the important new knowledge concerning the quantitative aspect of electrolytic processes, acquired in 1834 by FARADAY and embodied in the laws named after him, furthermore lacked apprecia-

³¹ *Lehrbuch der Chemie* III, 1, p. 71.

³² *Lehrbuch der Chemie* III, 1, p. 63.

³³ Basically BERZELIUS's mistake is of the same type as is made when one says: Inside it is 13°, outside it is 4°: we will therefore open the window, so that the 4° can also enter.

³⁴ For further, see W. HÜCKEL, *Theoretische Grundlagen der organischen Chemie*, Vol. II, p. 431 (5th Ed., 1948).

tion, not only by BERZELIUS, but by chemists generally, both then and also decades later. BERZELIUS himself went so far as to oppose this law because of a deeply rooted misunderstanding³⁵. He believed in fact that the same quantities of electricity appearing at the electrodes with the deposition of equivalent quantities of matter corresponded respectively to equal expenditure and gain in work. That stood in contradiction to his electrochemical theory of chemical affinity, since according to this the separation of the noble silver, for example, must demand a larger expenditure of work than the separation of the base electropositive lead. The error into which BERZELIUS and with him other investigators had here fallen lay in the belief that the yield of material at the electrodes was not fixed by the quantities of electricity alone, but that the electric potential was also a deciding factor. FARADAY's Law has nothing to do with chemical affinity; it is a stoichiometric law that expresses something concerning the relation between *quantities* of matter and *quantities* of electricity. If BERZELIUS wanted to learn something about chemical affinities he should have enquired into the relations between these chemical "forces" and the *potentials* which prevail in voltaic cells, or which are necessary to bring about the deposition of metals. This enquiry would subsequently have led to an extension of the potential theories relating to the quantitative aspect of the matter, and finally, in the manner to be described later, to the measurement of affinities for electrochemical processes with reference to a thermodynamical basis.

From the physical standpoint no experiments were then made to set about reshaping the Berzelian theory, perhaps because from the first the physical insufficiency of the picture sketched by BERZELIUS hindered physicists from occupying themselves with it more closely. Also perhaps because the various and manifest physical errors of BERZELIUS imbued them with little confidence in his theory, and the significance of the vague notion of affinity was not at all evident. When later the electrochemical concept was developed further and deeper from the physicist's standpoint by HITTORF, KOHLRAUSCH, HELMHOLTZ and others building upon the knowledge gained by FARADAY, this took place without reference to BERZELIUS. Therefore no true continuation of the thought processes of BERZELIUS are to be traced in this subsequent development, although the latter believed he had solved the problem of chemical affinity by his theory. Likewise neither ARRHENIUS's theory of electrolytic dissociation nor his theory of ions referred to it. Only R. ABEGG and G. BODLÄNDER about the year 1900 returned with their electropolar interpretation of valence forces to the road along which BERZELIUS had travelled.

Meanwhile attempts of quite a different kind were undertaken to make the concept of chemical affinity useful to science.

In the time following the reign of the electrochemical theory of

³⁵ Cf. W. OSTWALD, *Grundriss der allgemeinen Chemie*, p. 418 (5th Ed., Leipzig, 1917).

BERZELIUS, from 1840 onwards, the question of the cause of chemical affinity at first received scarcely a mention; nor did those supporters of the theory who still remained bring it into the foreground. The development of organic chemistry brought along with it a purely experimental enquiry into which atoms and groups of atoms could replace one another with preservation of the type of compound. The following up of this objective according to plan led by way of the theory of types to structural chemistry, whose dual foundation was the theory of atomic chains and the tetravalence of carbon, or, more generally, the saturation capacity of the atoms. The answering of the enquiry into the cause of atomic chains is renounced by structural chemistry, which indeed does not even attempt to relate this problem with that of chemical affinity. On the other hand, an attempt was made to link the other pillar of support of the structural theory, the idea of saturation capacity of the atoms, with the concept of affinity. Indeed, it even went so far as the identification of the two representations. Four units of affinity were spoken of for carbon, and affinity units for the other elements correspondingly³⁶. As the expression "unit" indicates, it was believed that in the number expressing saturation capacity, that is, the *valency*, a *measure* of chemical affinity had been found. In this the Law of Constant and Multiple Proportions appeared as an expression of chemical affinity. The electrochemical theory of BERZELIUS had left this law unexplained. Chemical affinity appeared therefore as if it were governed by fixed numerical ratios no: further enquiry was made into its physical cause.

Although it was now believed that a *measure* of affinity had become available, there was a complete lack of clarity concerning the kind of measurement and the physical significance of such affinity units. This is to be seen very clearly, for instance, in the definition of valency given by A. W. VON HOFMANN in his *Einleitung in die moderne Chemie*: "The expressions valency, mono-, di-, tri- and tetravalent, which indicate the combining powers of the atoms of the elements and the different degrees in which this power expresses itself in the various elements, originate from a comparative consideration of the capacities of the atoms for performing a certain work with one another". The differing degrees of atomic combining power here spoken of were, according to contemporary ideas, nothing other than varying degrees of affinity. Thus in the immediately subsequent period the words *valence* = *affinity* = *combining power* of the atoms were used side by side, mostly without definition³⁷.

The lack of schooling in physics of the contemporaneous generation of chemists was doubtless to blame for this vagueness in the concept. They were, generally speaking, unfamiliar with the exactness of a physically useful concept. Conversely, the current generation of physicists were also

³⁶ E.g., A. KEKULÉ, *Sur l'atomicité des éléments*, *Compt. rend.*, 1864, 58, 510; R. ANSCHÜTZ, *A. Kekulé II*, p. 352.

³⁷ See, in this respect, W. HÜCKEL, *Theoretische Grundlagen der organischen Chemie II*, pp. 430—431 (5th Ed., 1948).

not at all interested in the questions which so extensively occupied the chemists. For the physicist, the problem lay still further off the beaten track than had the problem of electrochemical dualism in its time. In both cases the vague nature of the concepts of the chemist must have repelled the physicist. A distinct gulf of this kind appeared in the collaboration between KEKULÉ and CLAUSIUS in Bonn which, in spite of personal friendship, did not come to scientific fruition. KEKULÉ lacked the requisite physical training³⁸; CLAUSIUS clearly had no desire in his contemplations of the structure of molecules to become absorbed in the thought processes of KEKULÉ³⁹.

Although physics was not then able to give a satisfying answer to the enquiry of the chemist into the cause of affinity, yet with better mutual contact a clearer definition of the basic concepts as well as a clear distinction of the hypothetical from the factual could have been attained. But as this was not brought about, many errors occurred in consequence. These could have been avoided if chemists had not from the beginning been breast-fed on the hazy concept of chemical affinity.

There were indeed investigators who were quite clear about the inadequacy of the usual mode of presentation. Thus LOTHAR MEYER⁴⁰ in his *Grundzüge der theoretischen Chemie* (1890) does not start with affinity but with the stoichiometric laws and the atomistic hypothesis. Affinity, the cause of which was still unknown, receives only a brief mention later in its relation to electrical attraction. The conclusion of this little work points again to the inadequacy hitherto of the ideas of an attractive force of affinity.

Completely independently of the structural chemists' comprehension of affinity and their "measure" of it were the attempts of the *thermochemists* to find an *energetic measure* of affinity. From the beginning these attempts forwent an explanation of the cause of affinity, but began instead with exactly measurable quantities, namely *heats of reaction*. A fundamental difference between this viewpoint and those held previously was that no mention was made of affinity between atoms, but rather of *affinity for certain chemical processes*. This viewpoint was introduced to science by J. THOMSEN in 1852, who saw in the heat developed in a reaction the expression of a "chemical force" acting in it as the propellant. Later M. BERTHELOT, from 1867 onwards, was of the opinion that every chemical reaction caused the formation of that substance whose formation evolved the largest quantity of heat, and thus also put affinity = heat of reaction. The incorrectness of this proposition is in point of fact proved by the existence of endothermic

³⁸ See, in this respect, R. ANSCHÜTZ, *A. Kekulé* I, p. 264. KEKULÉ had just exposed himself in CLAUSIUS' field of research, the mechanical theory of heat.

³⁹ R. ANSCHÜTZ, *A. Kekulé* I, p. 379.

⁴⁰ The outstanding physical schooling of L. MEYER in comparison to that of the other chemists of his time had already made itself apparent in 1865 in his criticism of A. KEKULÉ's article on the meaning of specific heat. *Z. Chem.*, 1865, [ii], 1, 250. R. ANSCHÜTZ, *A. Kekulé* I, p. 264.

reactions as well as by the existence of chemical equilibria. Nevertheless, the first step towards defining *affinity* as a measurable quantity of energy had been taken. A formulation of the definition of affinity free from inconsistencies was given in 1883 by VAN 'T HOFF in which he drew on the Second Law of Thermodynamics, thereby taking a path which A. HORSTMANN and B. RATHKE had indicated. The *free energy* (maximum work) became defined as a measure of the affinity of a process. The relations between this definition and BERTHELOT's principle, which as a general statement was false, were clarified in 1905 by NERNST in the formulation of his Heat Theorem.

This *thermodynamical definition* of affinity, now universally recognized, implies, however, something quite different from that which the older chemists understood by affinity. The question of the reason why atoms of certain elements enter into combination and others do not, which was the essential point for these chemists, is not answered by the thermodynamical definition. It is characteristic that M. BERTHELOT, the first to champion an energetic definition of affinity, rejected absolutely the atomistic theory. Thus for him the mock definition of C. L. BERTHOLLET, namely, affinity = forces of attraction between the smallest particles, meant absolutely nothing.

This mock definition which C. L. BERTHOLLET placed at the summit of his presentation and which later was to be repeated parrot-fashion again and again, was strangely enough only in part used as a foundation for his further discussions. As early as the second page he gives a concept of affinity quite independent of it when he says: "Every substance tending to enter into combination acts in proportion to its affinity and its quantity," and somewhat later: "The chemical activity of a substance depends not only upon the characteristic affinity of its constituents and the quantities, but simultaneously on the condition in which these constituents exist." In these statements lie latent the theory of chemical equilibria and with it also the VAN 'T HOFF definition of affinity. BERTHOLLET, who originally gave an atomistic pseudo-definition of affinity, was thus really a pioneer of the non-atomistic thermodynamical definition of affinity. This apparent contradiction is understandable when it is remembered that BERTHOLLET's atomistic conception of matter was pre-DALTON and originated in a philosophical need. BERTHOLLET did not derive the Law of Constant and Multiple Proportions from his atomistic conception of matter but, on the contrary, disputed it. He did not work solely with that which we designate as pure substances or as chemical compounds, but generally with equilibrium conditions in which all the reaction partners participate and in which pure substances present only limiting cases: "The various efforts to combine must be viewed as just as many forces which either unite to bring about a single result or partly neutralize each other by their opposition." Thus he here considered chemical processes as entities and not as the sums of elementary acts between fundamental particles (molecules), thereby referring affinity to these processes and not to the elementary structural units.

But this reference is now the same as that which later led to an exact thermodynamical affinity.

Something quite different had been accomplished with the thermodynamical definition of affinity from that which the atomists had intended. The position of equilibrium was given by the equilibrium constant, which in turn was derived, according to the NERNST Theorem, from the thermodynamical properties of the reacting partners. However, the real cause of the union of atoms to molecules and of the exchanges between chemical compounds in chemical reactions remained hidden.

As already mentioned, ABEGG and BODLÄNDER made the first steps towards the recognition of these causes about the turn of the century. They began with the relationships which existed between the valency of the atoms (the number of "affinity units"), their electrochemical behaviour and the Periodic System. In this they limited themselves, as did BERZELIUS at one time in his electrochemical-dualistic system, essentially to the interpretation of the relationships between inorganic compounds of a saltlike nature. The affinity was accordingly electroaffinity, and the "valencies" polar in nature; an element could employ, according to the circumstances, positive or negative valencies, and in such a way that the sum of all the positive and negative valencies for each element added up to 8. The less strongly pronounced were termed contravalencies, as, for example, the positive heptavalence of chlorine. Under certain circumstances, the latter did not operate at all, like the — hypothetical — negative heptacontravalence of sodium. Later (1906) ABEGG found himself obliged to accept, in addition to the *heteropolar* compounds which could be accommodated in his system of electroaffinity, also the *homopolar* compounds whose cohesion could not be explained by the ideas of electroaffinity.

It was possible to develop this concept of valence only after the cause of electroaffinity had been derived from atomic structure. In 1916, W. KOSSEL⁴¹, on the basis of the BOHR-RUTHERFORD model of the atom, developed a theory of heteropolar compounds which explained the favoured occurrence of fixed positive and negative valencies by a tendency of the atoms to form especially stable outer shells of electrons, rare-gas shells of eight electrons in particular. The cohesion of ions with stable outer shells formed by the assumption or relinquishment of electrons was believed to be effected by *electrostatic forces*. In this manner, the attractive forces effecting the cohesion between the atoms in combination made their appearance as the familiar COULOMB attractive forces. The cause of the "affinity" is the positive or negative electroaffinity of the atoms leading to the formation of ions.

KOSSEL's explanation of the formation of chemical compounds fails to work, as does that of ABEGG, for homopolar compounds, for compounds

⁴¹ W. KOSSEL, *Ann. Physik*, 1916, [iv], 49, 229.

between similar atoms — H_2 , Cl_2 , etc. — and for carbon compounds containing carbon chains. In order to take these compounds into account, G. N. LEWIS regarded the cause of chemical combination quite generally as the formation of stable shells of *eight* electrons, which do not always, as with KOSSEL, need to be realized in separated ions, but can also be brought into existence in such a way that one or more of the electron pairs are common to the atoms forming the compounds. According to this *octet theory*, every atom thus strives to surround itself with eight electrons. Thus, for example, the chlorine atoms in the chlorine molecule share one electron pair: $:\ddot{Cl}:\ddot{Cl}:$.

In sodium chloride, exactly as with KOSSEL, separated ions are present: $:\ddot{Na}:^+ : \ddot{Cl}:^-$.

The octet rule — the rule here concerned is one which can be broken only in certain cases — truly reduces the striving of the atoms for chemical combination to a common denominator (the formation of shells of eight), but states nothing concerning the cause of chemical affinity as such. Since the striving to fill up a shell of eight can be satisfied in different ways, namely by the formation of ions or by the sharing of electron pairs, these two types of activity of the electrons were differentiated by *electrovalence* and *covalence*. However, it was soon recognized that there were all sorts of transitions between the two. The cohesion of the atoms could be described in a simple physical manner only in the case of the heteropolar compounds held together by electrovalencies, namely electrostatic attraction of the ions as assumed by KOSSEL. As a supplementary idea, the assumption of a repellant force between the ions maintaining equilibrium with the attractive force at a fixed distance must however be added, for otherwise the ions would approach so near to one another that their electron shells would intermingle. In this description of the state of union of the atoms in heteropolar compounds, care must be taken to avoid seeing a physical cause of affinity in electrostatic attraction, since this attraction is only a consequence of the transference of an electron from one atom to the other. Since there is every kind of transition between homopolar and heteropolar compounds, it appears that such a transference can result in being more or less complete.

The *cause* of affinity, which formerly was denoted as an “attractive force” between the smallest particles, can only be ascribed to the interplay of valence electrons, which is able to assume various forms. For this the number as well as the kind of activity of the valence electrons plays a part. The restrictions governing the *number* very frequently comply with the octet theory, which in the last resort is an improved form of the ABEGG-BODLÄNDER concept of electrovalence and contravalence. The kind of activity lies between two extreme cases, homopolar bonding between identical atoms and heteropolar bonding or the “ionic link” in the typical salts. Here it must still be remembered that there are several types of homopolar

bonds⁴² — single, double, triple, semi-polar, and special cases such as, for example, the aromatic bond and the electronic activity in such molecules as N_2 and CO. "Affinity" assumes a special place in the case of metals for which the number and kind of activity of the valence electrons conform only in certain cases of compound formation to rules similar to those applying to the formation of other compounds, and for which generally other laws apply⁴³.

The *magnitude* of affinity bears no recognizable relationship to the type of linking of the atoms. The measure of it is given by the free energy of the chemical process. It is thus always the difference in free energy between the initial and final states, and in its measurement the conditions to which it refers must be specified. For example, when one speaks simply of the affinity between oxygen and nitrogen, one usually understands by this the affinity of the reaction $N_2 + O_2 = 2NO$, thus referring it to the elements in their molecular states. If one however wishes to define affinity as the "attractive force" between the atoms, then the free energy of the process $N + O = NO$ must be considered and this compared if necessary with the free energies of the processes $N + N = N_2$ and $O + O = O_2$.

It is clear that for a long time the multifarious problems included in the confused concept of a chemical affinity could not be correctly discerned, since science had not progressed far enough to answer them. Yet many wrong paths could have been avoided if from the first the atomistic and thermodynamical viewpoints had been clearly kept apart, or, in other words, the enquiry into the cause and the measurement of affinity had been separated. The split which, for a critical reader, became apparent in the first two pages of BERTHOLLET's book extended throughout chemical science for approximately a whole century. BERTHOLLET and all his successors placed atomistics at the heading of a viewpoint to which it did not belong. This was instinctively felt about a century later by the energeticists, who would have liked to see atomistics banned from science⁴⁴. At the same time, the idea of an "attractive force" between the smallest particles which led to compound formation was not in itself so erroneous. The atomist BERZELIUS had logically linked his electrochemical theory on to it. To be sure, it was unfortunate that not all compounds are polar-dualistically constructed, and that therefore an appropriate development of BERZELIUS's ideas, following a corresponding correction of his incorrect physical concept, was delayed for more than half a century.

Promising beginnings in the *measurement* of affinity were already quite possible in earlier times. For this, as already pointed out, VOLTA's

⁴² Concerning this, see Chapter VI: Chemical Bonds.

⁴³ Concerning this, see Chapter X: Alloys.

⁴⁴ It is noteworthy that OSTWALD neither in his *Grundlinien der anorganischen Chemie* nor in his *Grundriss der physikalischen Chemie* supplied an exact definition of that which he wished to be understood by chemical affinity. In introducing his teaching regarding affinity he says: Die Affinität ist die Ursache der chemischen Vorgänge" "(Affinity is the cause of chemical processes)".

electromotive series was suitable, even if polarization phenomena, then very incompletely investigated, had in part somewhat falsified the results. But apart from this possibility of development, which in the last resort would have derived from the affinity tables that which was to be deduced from them, a clear objective was already extant in the investigations of C. F. WENZEL, which, if correctly followed up, would have permitted the earlier fruition of knowledge that was first gained much later. WENZEL, in his attempts to measure the affinity of acids towards metals, determined the *rate of solution* of metals of similar surface in different acids. In this respect he remarked: "For if an acid dissolves one drachm of copper or zinc in one hour, an acid of half the strength requires two hours, provided the surfaces and temperatures remain the same in every case."

The idea of utilizing the velocity of a chemical process as an expression for the affinity had already been voiced before WENZEL. It is first found with PARACELTUS, who saw in the differing velocities of amalgamation of the metals an expression for their varying affinities, and again perhaps with STAHL when he arranged the metals in a sequence according to the "ease" with which they dissolve in acids. But nobody before WENZEL had indicated the quantitative aspect of the phenomena as clearly as he did when he enquired into the relationship between acid strength and velocity of solution. It makes no difference that we now recognize the thermodynamically defined affinity as not measurable by means of reaction velocities, but rather acknowledge the existence of fixed relationships between reaction velocity and thermodynamical affinity only in special cases: nor that WENZEL measured with the dissolution not the affinity of the acids towards the metals, which he really wanted to do, but actually the acid strength — that is, in modern language, compared the dissociation or affinity constants of the acids. His service consists in having been the first to state with full clarity the kinetic Law of Mass Action. Unfortunately, as already mentioned (p. 6), these investigations of WENZEL were to remain without response⁴⁵. It was not until 70 years later that WILHELMY took the same path in his investigations of the inversion of cane-sugar.

The enquiry into the cause of chemical affinity, so persistently pursued in discussions at a time when the question of a method of measuring it had not been answered, was much too prematurely opened. It was the pointless question *why?*, pointless because in science an answer to a *why?* can only be obtained when the question is connected with other already-solved problems. The question should then really not be: *Why?*, but more precisely should read: *With what is this or that connected?* As long as this more precise question cannot be asked, no answer will be obtained. Until

⁴⁵ How little WENZEL's accomplishment is known follows among other things from the fact that E. VON MEYER in his *Geschichte der Chemie* (Leipzig, 1895) presents WENZEL as only a forerunner of RICHTER, the discoverer of the Law of Constant Proportions, and does not mention at all his attempts to measure chemical affinity by the velocity of chemical processes.

one has advanced that far, one must be satisfied with the question *how?* Examples of this necessity are numerous in science. A very well-known example is the attitude taken by GALILEI towards the problem of free fall. He did not ask: *Why does the stone fall to the ground?*, but: *How does the stone fall?* If to the *why?* one supplies the answer: *Because it is attracted by the earth*, or: *Because it is heavy*, or: *Because of gravity*, the answer is only a circumlocution of the facts, which can be precisely expressed only in so far as, by mathematical description of the process of falling or of gravitational phenomena generally, that which one understands by gravity is exactly defined. No comprehension of the "nature" of gravity or of its "cause" is to be formed thereby, if by the "nature" of gravity one wishes to understand assertions which are not solely formulatable by mathematics. There is sense in asking after the "cause" of gravity only when it is attempted to relate it to other material properties. The indefinite question *why?* goes deeper than the question *how?* It allows a phenomenon to exist without relation to other phenomena in nature; but just because of this lack of relation no answer to it is to be expected. Only when definite relations can be conjectured is it possible to get any further with the question: *With what is that connected?* In the case of gravity, which has been exactly defined since NEWTON, it is only now possible to pose this question tentatively. In the case of chemical affinity the question *why?* was put still less definitely, because the concept of affinity itself was not at all clear.

It was BERZELIUS who with his electrochemical theory first enquired into the question of the connections. When later this theory was rejected, however, the discussion was referred back to the same basis as before BERZELIUS. It was not merely unfruitful but moreover even harmful to generations of chemists, for the latter were fed on it almost from the start and before they had learned to think of any clear chemical concept in an exact scientific manner.

The question *why?* which here appears with particular clarity as unscientific — for it *is* that from the scientific viewpoint, although SCHOPENHAUER presented it as the basis of scientific investigation — occurs frequently with people who take pains to get to the bottom of a thing, without realizing that for the time being they cannot see to the bottom and must therefore moderate their designs. Sometimes they would prefer not to concede to the latter point. Thus, if one wishes to advance in knowledge, a completely realistic attitude is not out of place. It is true that later, when knowledge has increased, this must not be allowed to mislead into complete disregard of the questions concerning the deeper connections.

CHAPTER II

THE BASIS OF SYSTEMATIZATION

1. General Systematization in Inorganic Chemistry

The wrestling with the problem of chemical affinity, as seen by the materially minded atomists rather than the energetically thinking thermodynamicists, shows that all attempts to explain this affinity and the chemical combination arising from it on a uniform basis were in vain. For that reason, no useful systematization of inorganic chemistry could have been evolved from these efforts. A uniform conception of the *structure* of inorganic *compounds* as a systematizing principle predominated for a time solely for the saltlike compounds in the electrochemical-dualistic system of BERZELIUS, the central idea of which later was unfortunately to pass for a long time into oblivion.

A comprehensive system in inorganic chemistry was developed on quite a different basis. Although "affinity" may here too be named as a principal theme, it deals with something quite other than chemical "electic" affinity, namely with an affinity in the original sense of the word involving a family relationship, and that too between *elements*. Chemically similar elements were arranged in groups or families. The triads of DÖBEREINER constituted the beginning (1817 and 1829). It was thereby recognized that within these groups there existed numerical relationships between the atomic weights of the elements included in them, in that the element in the middle of the triad possessed an atomic weight which lay almost exactly half-way between the atomic weights of the two other elements. But with the great diversity of the elements it was rather a long time before similar chemical properties and atomic weights could be arranged into a single ordered scheme. It was recognized, firstly by NEWLANDS in 1864, that on arranging the elements according to increasing atomic weight certain properties recur at regular intervals of usually eight elements, which he termed *octaves*. In 1869, the elements were brought by MENDELÉEF and LOTHAR MEYER into a general system that permitted the recognition of similar properties within certain families of elements, the *groups*, as well as of a regular change in properties with dependence on atomic weight. Both recognized independently of one another the essential principles of drawing up this *Periodic System*¹, namely the atomic weight and length of period. That not the atomic weight but the atomic number = place number in the system = number of charges

¹ The term *Periodic System* is not a fortunate one: for grammatical accuracy it must be called *System of the Periods*. To reduce it to one word, the expression *Period-system* has been suggested.

on the atomic nucleus had finally to be admitted as the governing factor is trifling as far as the nature of the systematization is concerned.

The essential point to be seen in the *systematization* created by the Periodic System is that it is one of *elements* and not of compounds. The properties of the compounds do not find a direct expression in it, and are only derived from more or less universally valid regularities within the individual groups and periods. It is to be regarded as a special success of the system that the *stoichiometric composition* of very many, though not all, compounds follows from the position of the component elements in the Periodic System. The valency of an element is equal to its group number. The varying valencies can also be deduced from the group number, at least for some of the elements on the right-hand side of the system, since a differentiation is made between the maximum valency towards oxygen and fluorine, which is equal to the group number, and the valency towards hydrogen which, when added to the group number, gives 8. The fact that for the rest, as far as the derivation of changing valencies and the valencies of the elements of group VIII are concerned, the Periodic System "breaks down", may here be mentioned simply as a reference to the fact that, as already pointed out, the system deals primarily with a systematization of the elements and is not a system of compounds.

This systematization of the elements makes possible a planned division of inorganic chemistry for instructional purposes. It had always been usual to treat one element after another. The order in which this took place was fundamentally immaterial as long as the presentation did not aim at comparing similarities. But since such similarities are incitement to further investigations, there were, even before the formulation of the Periodic System, viewpoints which governed the arrangement of the material and did not simply discuss the elements in the order of their initial letters or of their sequence in the atomic-weight table. The oldest viewpoint according to which a division of the elements was effected was a consideration of their *physical properties*, namely a division into *metals* and *non-metals*. It soon became apparent that, alongside of this division effected upon a *physical* basis, a subdivision according to the *chemical* standpoint was to be made. This became thoroughly useful. The same is true of the subdivision of metals into light metals and heavy metals. Within these large groups of elements families of the type of DÖBEREINER's triads provided a useful ordering of the material for comparative study. Nevertheless, there always remained a considerable arbitrariness in the arrangement of the remaining elements for teaching purposes.

This arbitrariness is removed when the Periodic System is employed as basis. The system presents the elements directly in families. Thus it is possible to deal with one group after the other. Relationships within the individual groups are exhibited most clearly when the main groups are all discussed first and then the subgroups.

Systematization in inorganic chemistry from the standpoint of the elements themselves is, it is true, *by no means the only possibility*, as the his-

torical development of text-book literature shows, although it is the most obvious and really useful one. This is to be seen from the fact that, among other things, a strict classification according to the Periodic System is by no means undertaken in all text-books. The reason for this is to be sought in the arrangement by groups of the Periodic System, according to which the relationships between neighbouring elements in the same period separated by the division into groups stand out less clearly than the relationships within each group; also in the numerous relationships which are neglected because of the imperfect nature of the Periodic System, as, for example, the close relationship between Al^{3+} and Fe^{3+} or Mg^{2+} and Fe^{2+} . This demonstrates clearly that the Periodic System is *unable* to give a complete *systematization of compounds*.

Commencing with the *properties of compounds* instead of the properties of the elements, a systematization on this basis is also possible. The inexperienced observer of the material world surrounding him will not trouble himself about elements but differentiate firstly between two large groups of substances, namely volatile and involatile. Here the boundary is of course as equally ill-defined as the differentiation into light and heavy metals: and there are transitions. On the whole, however, substances of chemically distinguishable character and, as we now know, completely different kinds of atomic linking are thereby separated from one another. A further subdivision of the involatile substances into those which, in spite of their low volatility and their high melting points, are more or less easily brought into solution and those which are practically insoluble is realized. A special place is allotted to the alloys, which possess the same metallic character as the elements from which they are prepared.

This large-scale differentiation can be comprehended more distinctly today and rather differently than appears to the naïve observer on account of our knowledge of the *types of linkage between the atoms*, or, as can be said in the language of former times, of the different forms of expression of chemical affinity. We know today that the forces which bind the atoms in compounds are of an electrical nature (for further details, see Chapter VI). There are links in which no or relatively little opposition of electrical charge occurs between the linked atoms. These are called *homopolar links*. In other cases strong opposing charges operate between the atoms causing the latter to appear directly as electrically charged particles. Such links are called *heteropolar links*. The volatile substances invariably contain atoms homopolarly bound and are *homopolar compounds*. The involatile substances are frequently compounds soluble in water with a saltlike character, and are *heteropolar compounds*. The involatile insoluble substances are also heteropolar in part, but are without real salt character, like the metal oxides and silicates. However, since there are also involatile homopolar substances, like diamond, for example, the scheme of differentiation given by direct observation, which does not recognize the state of bonding, can be relinquished,

and a differentiation made according to the following types of linkage without regard to volatility:

- substances with homopolar bonding of the atoms;
- substances with heteropolar bonding of the atoms;
- substances with metallic bonding of the atoms;
- substances with mixed bonding character.

Such a classification, which is quite independent of the elementary composition of the compounds, is by no means new. Rather it was already there, though unrecognized as a form of systematization, before anything was known concerning the composition of substances from their elements. The four elements of EMPEDOCLES and ARISTOTLE, fire, water, air and earth, nevertheless represent an incomplete classification of substances according to the principle of their properties. Being a physical phenomenon, fire does not belong here. In a certain sense water represents solutions and soluble substances, air the volatile and earth the involatile with silicate character². The principles of PARACELUS, sal, sulphur and mercury, again provide an even better classification of substances according to their properties and type of bonding³: *sal* the involatile heteropolar compounds, *sulphur* the more or less volatile and combustible homopolar compounds, and *mercury* substances of a metallic character (p. 15).

The division of substances according to their characteristic properties or, in modern language, according to the different kind of bonding between the atoms provides a cross-section through the inorganic world of matter differing from the usual one according to the elements and the Periodic System. In consequence of this, many connections stand out more sharply than usual. In particular, the varying nature of the problems in the methodical approach to inorganic research is much more clearly recognizable throughout the whole of its breadth than with the arrangement of matter according to the Periodic System. For example, the volatile, homopolar, inorganic substances, such as the silicon and boron hydrides, metal carbonyls, etc., (Chapter VII) appear together. For their investigation, a kind of structural-chemical thinking can be employed in part as for organic molecules. Saltlike heteropolar compounds and their solutions form a large field within which the methods of thinking and working predominating are the conception of ions and the application of electrochemical aids. Still other methods of research are demanded by the insoluble silicates, the refractory substances and the vitreous supercooled melts (Chapter IX). Structure investigation by means of X-rays and the ideas of crystal chemistry (Chapter VIII) concerning the spatial arrangement of atoms stand out here in the foreground. Next to the phase diagrams, as important in this case as in the former,

² The four elements can however be regarded as representatives of heat and the three states of matter.

³ Concerning the point that PARACELUS, in advancing his principle, intended something quite different from a systematization, see p. 2.

the same methods play an important part with alloys and intermetallic compounds (Chapter X).

If one element after the other is treated within the framework of the group of the Periodic System to which it belongs, only a small fraction of the large number of problems is met with each time. Sometimes few and sometimes many of these are touched, according to the nature of the element. As an example of an element, the discussion of which brushes up against a larger number of such problems, *vanadium* might be mentioned. Here the element itself, which serves for admixing with steels, demands a discussion of the problems of alloys for the specific case of vanadium steel. In doing this, vanadium carbide and nitride (Chapter X) will at the same time be appropriately included. The lower oxides of this element grant an opportunity to discuss metallic conductivity in oxides and the limits of the Law of Constant and Multiple Proportions (Chapter X), as well as change of valency and its significance for catalytic activity. The salts derived from the oxides invite a comparison with the salts of other metals of similar valency. For tetravalent vanadium, a comparison of the oxygen-containing cation vanadyl VO^{2+} is to be drawn with uranyl UO_2^{2+} . Vanadium pentoxide and vanadic acid form the starting-point for a discussion of colloid-chemical questions and the experimental results of aggregation of isopoly-acids in solution (Chapter III, Sections 6 and 7). Even an element which possesses only one valency can lead to an occupation with various kinds of inorganic problems. *Aluminium* may be selected as an instance ⁴. The production of the metal demands a treatment of the electrolysis of melts. The metal itself, because of its resistance to air in spite of its strong reducing powers, requires a study of strongly adhering, protective, superficial oxide layers. For its alloys, the commencement of submicroscopic separation of mixed crystal phases (Chapter VIII, 10) on hardening by the addition of copper in duraluminium must, among other things, receive consideration. In alums, aluminium salts lead to the problem of the isomorphism of aluminium with other trivalent metals. Aluminium hydroxide deserves special consideration because of its amphoteric nature, its aging phenomena, and its belonging to those oxides and hydroxides which actively change their structure in the course of time (Chapter XI, 8). The aluminium halides, in view of their double molecules, demand special examination concerning their structure and state of bonding (Chapter III, p. 167 ff). The great difference in the volatility of the fluoride in comparison with the other halides makes necessary a study of the problems of crystal structure, and in particular that of volatility (Chapter VII, 3). Quite different problems are touched by the aluminosilicates which, like clays and feldspars, for instance, possess quite different natures and can accordingly throw light on the problems of silicate chemistry from quite different angles (Chapter IX, 1).

⁴ Cf., in this respect, F. C. FRARY, *Adventures with alumina*, *Ind. Eng. Chem.*, 1946, **38**, 129.

For the beginner, such a presentation providing very different cross-sections of the problems of chemistry for the individual elements is, because of the diversity of the problems with respect to almost every element, as stimulating as it is instructive. He gains thereby, without becoming wearied, an impression of the richness of chemistry. If in the case of any element fewer problems are discussed, whether it be because these are to be found on the whole in smaller number than usual, or because they have already been dealt with for the other elements of the same group, then the chemistry of such an element will appear "monotonous", as, for example, that of zirconium, rubidium or caesium. On the other hand, it is precisely the diversity of the problems found for many elements which provides the reason why, in spite of the ordered principle existing in the Periodic System, so many beginners deem inorganic chemistry much more difficult to learn than organic. In the latter there is only *one* problem which for him exists entirely in the foreground, and that is the structure of the molecule according to the same invariable principles of planned synthesis and planned degradation. This is only the case in inorganic chemistry as long as one limits oneself to electrolytes which, for the beginner, are admittedly of special importance and must therefore receive preferential treatment. However, as soon as one passes on to other classes of matter, it becomes apparent that the whole problematical element in inorganic chemistry has essentially many more aspects than appears from a mere consideration of the saltlike substances. Systematization of the elements can, on going deeply into the matter, act as guide only to a limited extent, since with every element the most diverse problems come up for discussion. This shows that the Periodic System alone does not make it so easy to find one's way through inorganic chemistry.

Where a comparison of the compounds of one element is made with the corresponding compounds of another, the Periodic System nevertheless gives the most valuable guiding-lines for the planned procurement of important observational material. In this direction, W. BILTZ and his school, more particularly in *Beiträgen zur systematischen Verwandtschaftslehre* (see, for example, p. 319), knew how to make the most of it. It has also guided W. A. ROTH in his thermochemical investigations of inorganic compounds (Chapter XI, 1). But it is not the only way for an investigator in inorganic chemistry. He can also allow his path to be indicated by the manifold problems that exist in inorganic chemistry in consequence of the different types of atomic linkages and the different atomic structures. From the point of view of learning, this way is unquestionably more difficult than the other ⁵.

⁵ In consequence, there is scarcely a text-book in which the matter is arranged according to the viewpoint of material properties or kinds of bonding. The first attempt in this direction was probably made in G. SCHWARZENBACH's *Lehrbuch der anorganischen Chemie* (Thieme, Leipzig, 1941). Because of the brief presentation and the strong tendency towards expression by formulae, the manifold nature of the problems with the many-sided methods of dealing with them is by no means shown to its full advantage.

2. The Systematization of Saltlike Inorganic Compounds

A universally accomplishable systematization of inorganic compounds encounters difficulties which, as we now know, have their origin in the fact that the chemical bond can be effected by differing kinds of interactions between the atoms of a compound. It is therefore profitable to commence with a broad type, develop a systematization for this, and then see how far it is applicable to compounds not belonging to the same type. Since, among the inorganic substances, *salts* were the first type of compound to receive an especially thorough investigation of their properties and reactions, they were taken as the starting point for the creation of the systematization, that is, special attention was given to their predominating relationships.

The first attempt at a general systematization of inorganic compounds was undertaken by BERZELIUS in the year 1820. In accordance with the existing state of knowledge, it had to be built on the experiences gained from salts, although BERZELIUS by no means wished to limit himself to this class of compound. The basis of his systematization still lives in the terms *compounds of the first and higher orders*. These expressions were originally employed by DALTON⁶, although, it is true, in a sense other than used by BERZELIUS. DALTON's attempt at a classification of chemical compounds, the oldest of its kind, was purely schematic, for DALTON divided them according to the sum of the relative numbers of atoms occurring in the compounds. An atom of an element was according to him an atom of the first order, the compound AB an "atom" (DALTON was not yet to know the concept molecule) of the second order, the compound AB₂ or A₂B or ABC an "atom" of the third order, and so on. With BERZELIUS⁷, it was not the total number of elementary atoms but the number of species of elementary atoms which fixed the order. By compounds of the first order, BERZELIUS understood binary substances, that is, those consisting of two elements irrespective of the proportional numbers of atoms within them. To these "compound atoms" of the first order, as he called binary compounds, belong substances of the formulae AB, AB₂, A₂B₃, A₃B₄, etc. Compounds of higher order arise by association of compounds of the first order according to the Law of Constant and Multiple Proportions, for example, CaCO₃ from CaO + CO₂, K₂SO₄ from K₂O + SO₃. A compound of the third order consists of two compounds of the second order. As an example of a compound of the fourth order, BERZELIUS cited alum, being a combination of the third order compound K₂SO₄·Al₂(SO₄)₃ (= K₂O·Al₂O₃·4SO₃) with the first order compound 24H₂O. But BERZELIUS did not always apply this kind of classification consistently. The double salt schoenite K₂SO₄·MgSO₄·6H₂O, arising by the union of the two salts with water of crystallization, belongs, according to BERZELIUS, along with alum to the fourth order, whereas the quite analo-

⁶ J. DALTON, *New System of Chemical Philosophy* I, pp. 212, 213.

⁷ J. J. BERZELIUS, *Théorie des Proportions Chimiques*, p. 17 (1835).

gously arising double salt carnallite $\text{KCl.MgCl}_2.6\text{H}_2\text{O}$ belongs to the third. However, such inconsistencies in classification remained without detriment to the further development of knowledge, because a schematic arrangement of compounds in classes of different order for the purpose of obtaining a useful survey was never undertaken.

Indeed, the formal classification of BERZELIUS, which WERNER first brought to life more than 50 years later in his co-ordination theory, did not play an especially useful part in inorganic chemistry, although the dualistic principle underlying it did. BERZELIUS likewise tried to give this principle a theoretical foundation in that, in his electrochemical theory already discussed (p. 29 ff), he gave an explanation of the cause of cohesion of atoms in binary compounds, as also of the union of these to compounds of higher order. From the theory of opposed electrical charges, the dualistic principle was bound to follow. Apart from the physical electrochemical basis, it was essential for this dualistic interpretation of systematization that a certain continuity or independence be ascribed to compounds of the first order in building up compounds of higher orders, similar to that ascribed to atoms in compounds of the first order. This idea was by no means artificial, but suggested by the chemical behaviour of double salts, which in solution react as a stoichiometric mixture of two single salts, as well as by salts containing water of crystallization. Indeed, still more is achieved by this kind of subdivision of compounds of higher order. That is, it frequently corresponds to the manner of formation and decomposition of salts of the oxy-acids like, for example, calcium carbonate, CaO.CO_2 . The salts of the oxy-acids appeared thereby to be placed analogously to double salts such as KCl.MgCl_2 and the compounds now distinguished from them as complex salts such as 2KCl.PtCl_4 . The binary classification of salts of the oxy-acids was also suggested by their chemical reactions which, as with salts of the first order, appear as the reactions of two largely independent components. Their formation from acid and base is also in accord with this, since the acid was to be thought of as a compound of the second order and composed of acid anhydride plus water, the base analogously of basic anhydride plus water.

Thus in "solving" the straightforward chemical formula of a compound according to the principle of binary analysis, it followed that the formula was permitted to state more than the stoichiometrical composition for which, as a brief expression, it was originally intended. The solved formula of a compound became a *reaction formula* indicating the way the compound reacted.

However, such a dissection could not always be carried out without contradiction. BERZELIUS was already clear about this. The thermal decomposition of ammonium nitrate into nitrous oxide and water, for example, which is of course irreversible, in contrast to the thermal decomposition of calcium carbonate, is not suitable for solving the formula of ammon-

ium nitrate as a compound of the second order according to the scheme $N_2O \cdot 2H_2O$. Rather its manner of formation from ammonia and nitric acid appears here to justify the style $NH_3 \cdot HNO_3$, which in other ammonium salts corresponds to decomposition into ammonia and acids at elevated temperatures.

In writing ammonium nitrate as $NH_3 \cdot HNO_3$ and similarly for the other ammonium salts, the pronounced analogy which indubitably exists with the salts of the alkali metals, especially of potassium, was not apparent. In particular, an analogous formulation of the salts of hydrochloric acid was not possible. Potassium chloride KCl appeared as a compound of the first order which did not contain the acid HCl from which it is formed on neutralization, while ammonium chloride as a compound of the second order $NH_3 \cdot HCl$ showed hydrogen chloride to be one of its components. In the course of time, examples were multiplied indicating that a consistent application of binary analysis for the illustration of reactions was not possible, although in many cases it corresponded to the requirements of a reaction formula.

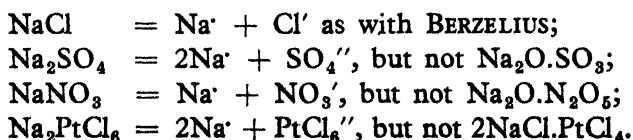
Yet it is not correct to reject the systematization of inorganic chemistry according to binary analysis altogether. It fits for far too many cases. By all means, in order to appreciate its usefulness and the limits of its applicability, a theoretical reason had to be produced which was able to present the connection between binary structure and ability to react. BERZELIUS had already provided such in his electrochemical-dualistic theory. This sees the cause of the binary structure in an electrical attraction of oppositely charged particles — atoms in the case of compounds of the first order, and compounds of the first order in the case of compounds of higher order. The theory could not be maintained in this form because the compounds of the first order associating to compounds of higher order are electroneutral in form, BERZELIUS having however attributed a charged character to them (p. 30). An addition of the electronegativity and electropositivity of the atoms in compounds of the first order, as BERZELIUS accomplished it in order to be able to explain the cohesion of the latter among themselves, is inadmissible from the physical standpoint. Nevertheless, the results of electrolysis indicated opposing charges of some kind and appeared for compounds such as K_2SO_4 , for example, to justify the formulation $K_2O^+SO_3^-$, $2KOH$ ($= K_2O + H_2O$) appearing at the negative pole and H_2SO_4 ($= SO_3 + H_2O$) at the positive. On the other hand, BERZELIUS had to forgo experimental support completely in suggesting a corresponding polar formulation for the formation of alum, which was supposed to be a consequence of the compensating of the positive electricity of K_2SO_4 and the negative electricity of $Al_2(SO_4)_3$. The assumption of a polar cohesion between the single salts in the double salt is here no more justifiable from the results of electrolysis than it is experimentally supportable in non-electrolytes. Thus BERZELIUS, to the detriment of his theory, was led perforce to very daring physical hypotheses⁸.

⁸ *Lehrbuch der Chemie* III, 1, p. 71 ff.

The basic idea to which BERZELIUS was led by the behaviour of acids, bases and salts on electrolysis, namely that there is opposite electricity in the substances which causes the cohesion and stipulates a binary structure, was however incorrect. BERZELIUS made the mistake, which nevertheless can be easily forgiven, of comparing this binary structure existing in numerous cases on an electrical footing, as in the salts of the oxy-acids, with the splitting up of a substance into two parts on thermal decomposition. The reaction formula based on the latter, as we now know, is *not* suitable for an understanding of the electrical relationships between the atoms in a compound, and is therefore not to be regarded as a universally valid and *unequivocal* reaction formula.

The true state of affairs was first summarized by ARRHENIUS in 1884 in his theory of electrolytic dissociation, according to which acids, bases and salts dissociate into *ions* in melts and aqueous solution. The big step forward made by this theory exists less in the fact that ARRHENIUS assumed a dissociation of electrolytes into ions, than in the recognition of *which* atoms and atomic complexes appear as ions in aqueous solution or in the melt. The idea of ions, already found with FARADAY and, indeed, to a certain extent still earlier with GROTHUS, was successfully utilized by physicists for the explanation of processes during electrolysis long before ARRHENIUS, as in 1853 by HITTORF for the explanation of transport numbers and in 1876 by KOHLRAUSCH for the understanding of the relations extant in electrolytic conductivity. But the investigators did not concern themselves with the material nature of the carriers of the electricity during electrolysis. The recognition of these is due in the first place to ARRHENIUS, who was moreover able to show that the electrolytic dissociation of salts and many acids and bases was much more extensive — namely almost complete — than one was formerly inclined to assume.

ARRHENIUS freed himself from the idea that the oppositely charged units had to be prepared as uncharged substances or, in the event of this being possible, that the properties of these substances were in any way similar to those of ions. In the binary salts the ions are identical with the units also assumed by BERZELIUS. In the salts of the oxy-acids, on the contrary, they differ from these. Thus all sodium salts contain as a structural unit the sodium as Na' , irrespective of whether they are compounds of the first or higher order according to BERZELIUS, the salts of oxy-acids, of halo-acids or double salts. The compound ions occurring in the compounds of higher order are generally not obtainable in the uncharged state, but are decomposed by the water on delivering up their charge at the electrode. The structures of the following are thus:



As *reaction formulae*, the formulae of ARRHENIUS are from the first as justifiable as those of BERZELIUS. They are reaction formulae for *formation* and *decomposition* in aqueous *solution*, while the latter are valid for thermal formation and decomposition. The ionic formulae, however, are to be preferred, in that the cohesion of the structural units, which are oppositely charged, thereby appears in theory to be the result of known physical forces. From the experimental standpoint, to be sure, this preference consisted for the time being only in the consideration of the reactions of acids, bases and salts in solution, and the question of the situation in the pure crystallized compounds remained open.

It is obvious to assume that the ions, which effect the transport of charge in aqueous solution or in the melt, already exist in the crystals. Admittedly there was for a long time a lot of coming and going before the ionic theory also came to be applied in this latter implication to the crystalline state, if only because there was too much prejudice in favour of the notion that crystals are built up from molecules corresponding to the formula of the compound. The results of X-ray analysis of inorganic compounds led generally to a different conception of the structure of the crystalline state. (Quite unnecessarily, it was simultaneously thought that the applicability of the molecule to the crystalline state had in general to be fundamentally denied.) Doubtless individual investigators had previously had the right conception of the building up of crystals of saltlike compounds from ions⁹.

With the assumption of ions in the crystal lattice, the older view of BERZELIUS, that on the formation of a compound opposing charges neutralize one another, had of course to be given up, and indeed reversed. The opposing charges are formed on compound-formation, and as such are completely developed within the crystal¹⁰, so that the cohesion of the ions can be described by means of electrostatic COULOMB forces. If one speaks of sodium, for instance, as an electropositive and chlorine as an electronegative element, one does not mean, as did BERZELIUS, that a sodium atom possesses positive electricity and a chlorine atom negative electricity, but that a sodium atom endeavours to become positively charged and a chlorine atom negatively charged.

Electrolysis provided for BERZELIUS the experimental background of his electrochemical theory. It did not, as he believed, reflect the electrical nature of the atoms but of the *ions* already formed complete. Hence the formulation of the theory of electrolytic dissociation by ARRHENIUS meant something more than a mere linking up with the old thought processes of BERZELIUS. By it, rather, the ideas of BERZELIUS were to a certain extent correctly reordered, that which had stood in the wrong place being brought into correct align-

⁹ Thus, for example, A. HEYDWEILLER had ascertained that the molecular refraction of salts in the crystal and in aqueous solution was nearly the same, that is, that ions are also to be assumed for the solid state. *Ann. Physik*, 1913, [iv], 41, 519.

¹⁰ In the crystal they are even more perfect than in the stable salt molecule at high temperatures, as the diminishing of the interatomic distance on the volatilization of a salt shows. As deformed ions, Na and Cl are closer in the NaCl molecule than in the strictly heteropolar lattice (Chapter VIII, 7, (iv)).

ment. The opposition which **ARRHENIUS** first encountered, in spite of the preliminary work of **FARADAY**, **HITTORF**, and **KOHLRAUSCH**, probably had its origin partly in this rearrangement of ideas which were familiar in the older electrochemical theory, but to a greater degree apparently in the fact that the theory, although not completely, yet very largely broke with the idea of molecules of acids, bases and salts existing in solution.

On turning away from the electrochemical theoretical basis and considering only the dualistic principle as it necessarily results from the electrochemical theses of opposing charges of both **ARRHENIUS** and **BERZELIUS**, one cannot fail to recognize the advance which the **ARRHENIUS** viewpoint meant for the systematic formulation of saltlike compounds. The preference for splitting up into *ions* according to **ARRHENIUS** rather than splitting up into basic and acidic oxides according to **BERZELIUS**, is brought out clearly by the fact that all the salts of the same metal now contained the same metal ion, and that the reactions they have in common became the reactions of this ion. According to **BERZELIUS**, on the other hand, sometimes the metal, sometimes its oxide, and sometimes its chloride is to be regarded as the structural unit (see the previously mentioned comparison for a number of sodium salts), the common reactions being understood only after splitting up the oxide and chloride respectively. The special case of ammonium salt in which, according to **BERZELIUS**, one component was always an acid, disappears with **ARRHENIUS**. Thus, for example, $(\text{NH}_4)_2\text{SO}_4$ contains "the same SO_4 " ion as Na_2SO_4 . The compound ammonium ion NH_4^+ becomes analogous to the alkali ions.

The composition of the non-elementary ions appearing on electrolytic dissociation received as little consideration by **ARRHENIUS** as by **OSTWALD**, whom the scientific world has in particular to thank for the rapid expansion of **ARRHENIUS**'s theory. Rather it was accepted as a fact. In this respect it appears striking, on an unprejudiced consideration of their composition, that the anions of the oxy-acids commonly contain four and less often three oxygen atoms, while other numbers occur much less frequently. The pyro-acids possess seven oxygen atoms on two other atoms throughout. These numbers stand in no visible relationship with the valency of the element forming the oxy-acid. **ALFRED WERNER** in his *co-ordination theory* recognized how to combine these striking relationships with observations concerning the composition of complex salts, and how to utilize them for a systematization comprising a large proportion of the inorganic compounds.

3. The Co-ordination Theory

(i) The Foundations of the Theory

In the development of his co-ordination theory, **WERNER** was guided by the idea of a definite spatial arrangement of the atoms. A similar *stereochemical* viewpoint had meant a fruitful development of the structural

chemistry of organic compounds and had led to the explanation of isomerism until then not explicable. In this manner, WERNER himself, in collaboration with HANTZSCH, was able correctly to interpret the isomerization phenomena of the oximes. Furthermore, in the application to inorganic compounds of the stereochemical way of thinking, WERNER freed himself from the structural-chemical viewpoint which, in the case of organic compounds, had to be connected with the stereochemical. He abandoned completely the principle of the formation of atomic chains, attempts having been made on previous occasions, but without proper success, to utilize this principle for inorganic chemistry. Rather, the characteristic of the co-ordination theory is a *centralized* construction of the system under consideration, with special attention directed to the *central atom* as, up to a certain point, the main atom about which the other atoms or groups are *arranged — co-ordinated —* or subordinately group themselves in some definite way. About the year 1860, KOLBE had attempted to form a similar conception of the structure of organic compounds according to a kind of monarchical principle, but foundered because in these the members of a carbon chain do not allow a privileged place being assigned to one of the atoms contained in it, it being therefore arbitrary to select one. However, for many inorganic compounds in which, as in the acid radicals, unlike atoms of usually only two kinds are joined together, the selection of one as a central atom is to be justified.

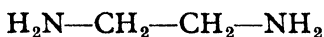
WERNER derived the especial significance of the central atom from the composition of complex salts without going into any special stereochemical idea. The ammoniates of trivalent cobalt, named *cobaltammines* by Werner, and other complex compounds of cobalt served him as examples. The experimental basis of the theory was the same as that of the theory of electrolytic dissociation according to ARRHENIUS, namely specific ionic reactions, electrical conductivity and the determination of molecular weights in aqueous solution.

Three ammoniates of trivalent cobalt are obtainable from an ammoniacal solution of cobaltous chloride on oxidation with atmospheric oxygen, namely $\text{CoCl}_3 \cdot 6\text{NH}_3$, $\text{CoCl}_3 \cdot 5\text{NH}_3$ and $\text{CoCl}_3 \cdot 4\text{NH}_3$, from which the ammonia cannot be directly expelled by alkali, that is to say, it must be very firmly bound. $\text{CoCl}_3 \cdot 6\text{NH}_3$ precipitates all of its chlorine with silver nitrate as silver chloride, exhibits a specific molar conductivity corresponding to dissociation into four ions, and gives a freezing-point depression about four times as large as the molecule $\text{CoCl}_3 \cdot 6\text{NH}_3$ should have. On electrolysis the ammonia wanders with the cobalt to the negative pole. The salt is therefore to be written $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ and dissociates in solution into the hexammine-cobaltic ion $[\text{Co}(\text{NH}_3)_6]^{3+}$ and $3\text{Cl}'$. Corresponding experiments with the salt $\text{CoCl}_3 \cdot 5\text{NH}_3$, which precipitates only two-thirds of its total chlorine with silver nitrate in the cold, lead unequivocally to the formula $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$, which corresponds to dissociation into the chloropentammine-cobaltic ion $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ and $2\text{Cl}'$. The salt $\text{CoCl}_3 \cdot 4\text{NH}_3$

precipitates only one-third of its chlorine with silver nitrate in the cold, and in agreement with this the other experimental results also lead to the formula $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ and a dissociation into the dichlorotetrammine-cobaltic ion $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ and Cl^- .

In all these salts cobalt is linked to six atoms or groups. The meaning of the number 6, the *co-ordination number*, is immediately obvious. The same number 6 is also found in the unusually numerous other complex compounds of trivalent cobalt, and, in point of fact, not only in those which have the cobalt in the cation but also those containing the cobalt in the anion, like $\text{Co}(\text{NO}_2)_6'''$, $[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]'$, or $\text{Co}(\text{CN})_6'''$. The co-ordination number 6 thus proves itself to be independent of the nature of the attached groups. (In other cases a dependence on the latter as well as on the temperature has been established — see later.) The groups may be neutral molecules like NH_3 or H_2O , or acid radicals such as the halide ions SO_4'' , NO_2' , $\text{C}_2\text{O}_4''$, etc. In the nomenclature, NH_3 is denoted as *ammine-*, water as *aquo-*, and the acid radicals by the attachment of the letter *o*, for example *chloro-*, *sulphato-*, *oxalato-* or, generally, *acido-*. The trivalent cobalt atom thus takes up the same position in relation to the most varied groups, it being only natural to regard this position as central and select it accordingly as the *central atom* with *co-ordination number 6*.

Sometimes, it is true, instead of the number 6 a smaller number is encountered. However, among these exceptions a special constitutional peculiarity of one or more of the groups is invariably to be ascertained, namely the presence of two functional groupings. Thus ethylenediamine



is able to take the place of two ammonia molecules or, as usually expressed, occupy two *co-ordination positions*: similarly the oxalato group $\text{OOC}-\text{COO}$. Without making any forced assumptions it is always possible to talk of six co-ordination positions for cobalt and hence of its co-ordination number 6.

A connection between the co-ordination number and the valency of the central atom does not exist, since divalent cobalt in hexammine cobaltous chloride $[\text{Co}(\text{NH}_3)_6]\text{Cl}_2$ also exhibits the co-ordination number 6. Potassium ferrocyanide $\text{K}_4[\text{Fe}(\text{CN})_6]$ with divalent and potassium ferricyanide $\text{K}_3[\text{Fe}(\text{CN})_6]$ with trivalent iron constitute a further example of this.

The approach of an electroneutral molecule to the central atom makes no change in the charge of the ion, while acido groups reduce the ionic charge by an amount corresponding to the charge they would otherwise bear as ions. If both numbers of charges are equal, a *non-electrolyte* results, like, for example, $(\text{H}_3\text{N})_3\text{Co}(\text{NO}_2)_3$. If the number of charges on the acido groups is larger than the charge on the central atom, an anionic complex occurs, for example, $[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]'$ or $\text{Co}(\text{NO}_2)_6'''$.

The co-ordination number 6 is very wide-spread in complex compounds. But other co-ordination numbers occur, although not with trivalent cobalt.

The co-ordination number 4 is also encountered frequently, 3 less commonly, 2 is already fairly rare as is also 8, while 5 and 7 hardly occur at all. The co-ordination number 4 is found more especially in the anions of the oxy-acids — for example, SO_4'' , CrO_4'' , PO_4''' , ClO_4' , MnO_4' , MnO_4'' — among which the co-ordination number 3 is of course often met with — for example, CO_3'' , NO_3' , ClO_3' — these numbers also being well-known in the complex salts, like, for instance, $\text{Cu}(\text{NH}_3)_4''$, $\text{Au}(\text{CN})_4'$, $\text{Cu}(\text{CN})_4''$ and CuCl_3' . The oxy-acids, as far as the structures of their anions are concerned, fit structurally into the framework of the usual compounds characterized as complex compounds, and thus enter into analogy with the halo-acids. Here the co-ordination number 6, almost absent in the case of the oxy-acids (periodic acid H_5IO_6 being a rare exception) is more frequently met with than the co-ordination number 4 or perhaps 3 — SiF_6'' , PtCl_6'' , PtCl_4'' , CuCl_3' .

For a particular central atom, the co-ordination number is not always invariable throughout. It may depend on the nature of the groups as well as the experimental conditions under which the compound is prepared. For monovalent copper, for instance, the cyano-complexes $\text{Cu}(\text{CN})_2'$ and $\text{Cu}(\text{CN})_4'''$ are known, and for divalent copper, $\text{Cu}(\text{CN})_4''$, as well as the chloro-complex CuCl_3' ; silicon has towards oxygen in the silicates the co-ordination number 4, towards fluorine in the fluosilicates the co-ordination number 6. The amines of calcium chloride, where the compounds $[\text{CaNH}_3]\text{Cl}_2$, $[\text{Ca}(\text{NH}_3)_2]\text{Cl}_2$, $[\text{Ca}(\text{NH}_3)_4]\text{Cl}_2$ and $[\text{Ca}(\text{NH}_3)_6]\text{Cl}_2$ are known, constitute a specially instructive example of the change in co-ordination number of a central atom¹¹.

(ii) The Co-ordination Number

The frequency with which the co-ordination numbers 6, 4 and 3 occur, for which a symmetrical arrangement of the groups in the space around the central atom is possible, while groups of 5 and 7 cannot be fitted into spatially equivalent positions¹², permits the conclusion that very strong spatial considerations are determinative in fixing the co-ordination number. Support for this is found in the fact that only the co-ordination numbers 4 and 3 occur for the elements of the first period, while the number 6 appears only when we get to the elements of the second period. In the former case the central atom is so small that there is not room for more than four groups around it. This conception immediately suggests itself if the complexes are *thought of as being built up of rigid ions*, but is not adequate, since, according to it, the co-ordination number 8 should occur for central atoms of large radius much more frequently than is in fact observed. The co-ordination number 12, which plays such an important part in the lattices of

¹¹ Concerning the change in co-ordination number of aluminium in the crystal lattice from 4 to 6 with respect to oxygen, so important for the chemistry of silicates, see Chapter IX, Part I, 1.

¹² The *planar* regular pentagon and heptagon are here disregarded.

metals, could likewise occur for very large central atoms. The limitation of the groups generally to 4, and from the second period onwards generally to 6, must thus be due to yet other reasons. These are arrived at by starting with a model of a complex constructed from rigid ions, and regarding the bond between the central atom and a surrounding unit as a homopolar bond effected by an electron pair. On counting the number of bonding electrons surrounding the central atom, a group of 8 electrons, an octet, is obtained for 4 units, for 3 units only 6, a sextet, and for 6 units a group of 12 electrons. Indeed, for compounds of the first order, whether these be heteropolar or homopolar, the formation of an octet is of special significance on account of the stability of a shell of eight electrons. Furthermore, the number of electrons in the outer shell, for theoretical reasons which are given by the quantum theory of atomic structure (p. 270), is limited to a maximum of 8 for the first period of the Periodic System. Thus an atom of an element from this period escapes the possibility in a complex compound of surrounding itself with more than four units bound by electron pairs.

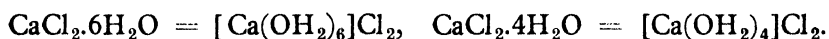
For elements of the second period, the number 8 can be exceeded, although comparatively rarely, and increased to 12. This follows from the existence of several compounds of the first order, namely PF_5 , PCl_5 and SF_6 . For a time it was believed that the strict validity of the octet rule must also be assumed for these compounds, and a formulation was looked for which complied with this rule. But it is now known that this is not correct, and that here also up to 12 electrons can in fact occur in the outermost shell. Accordingly, the complex ions of the elements of this period containing six groups, as also those of the next period, are to be formulated with a set of 12 electrons, like, for example, AlF_6''' , SiF_6'' , $\text{PF}_6'^{13}$, $\text{AsF}_6'^{14}$, $\text{SbF}_6'^{14}$, SnCl_6'' , etc.

According to these views, the valence electrons of the central atom are combined with those of the valence electrons contributed to the bond by the attached units into a grouping which, as far as the number of the electrons is concerned, is to be compared with the outermost electron shell of an atom. Notwithstanding, the central atom does not always contribute electrons to the bond with an attached unit, since no valence electrons from the central atom are demanded by those groups which themselves supply an electron pair, like the pair on the oxygen in water and the nitrogen in ammonia. Consequently, such units are even able to attach themselves to central atoms which possess a stable outer shell of eight electrons, like the ions of the alkali and alkaline-earth metals. In such cases, it is not fitting to include these eight electrons with the lone pairs of the groups, but instead to group the latter by themselves. It is then immediately comprehensible why the groups in this case, where the pairing of electrons between the groups and

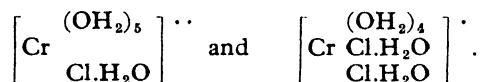
¹³ W. LANGE, *Ber.*, 1928, **61**, 799; W. LANGE and EMIL MÜLLER, *ibid.*, 1930, **63**, 1058.

¹⁴ C. MARIGNAC, *Liebigs Ann. Chem.*, 1868, **145**, 243.

the central atom is lacking, are not specially firmly bound, and why in consequence the co-ordination number is not so exclusively fixed as when a stable shell results from interaction between the valence electrons of the central atom and of the groups. This is quite in agreement with experiment. The water of crystallization of the salts of the alkali metals and alkaline-earths can vary, as follows from the existence of different hydrates of these salts which may be regarded as aquo-salts; for example,



Likewise there are several ammines of calcium chloride with different numbers of ammonia molecules. These have already received mention. Complexes of this kind, within which the groups to a great extent retain their individuality, are named *addition complexes*. The water bound to anions with completed shells, for example, to SO_4^{--} , is also not particularly firmly held; the same is true of that bound to acido groups with completed shells inside a complex, such as the water molecules attached to the non-ionizable chlorine in the chromic chloride hexahydrates



The lone pairs on groups such as water and ammonia, however, are often to be included with the valence electrons of the central atom. That is to say, if the latter does not possess a stable outer shell, it is just as conceivable that these electron pairs, like the pairs binding the other groups, join themselves into a shell with the valence electrons, as it is that they remain outside. The formation of a combined group is thus always especially favoured if the number of electrons obtained thereby corresponds to the number of electrons in a stable shell¹⁵.

This striving to form a shell of this kind is the reason for the constant occurrence of the co-ordination number 6, as in the complexes of trivalent cobalt, for example. The cobalt atom possesses 27 electrons of which 7 + 2 are in the still uncompleted outermost shell¹⁶. On forming the trivalent cobaltic ion a total of 24 of these remain, 6 being in the outer shell. 12 electrons are added by the attachment of 6 groups supplying the necessary electron pairs for the bonds, such as ammonia molecules and non-ionically bound chloride ions or other acido groups entering into the inner sphere. If these are collected with the first 6 into a group of 18 and this group is subdivided into 10 + 8 electrons, then the shell arrangement of the rare gas krypton is arrived at, having a stable shell of 8 as its outer shell and 36 as its total number of electrons. This is equal to the 24 electrons on the cobalt ion plus the 12 bonding electrons of the groups inside the complex.

¹⁵ N. V. SIDGWICK, *J. Chem. Soc.*, 1923, 123, 725.

¹⁶ In this connection, see the table in Chapter IV, p. 271.

Such complexes within which the valence electrons of the central atom form common shells with the electron pairs binding the groups are characterized as *penetration complexes* after W. BILTZ and W. KLEMM¹⁷. As is readily comprehensible, they are especially stable. To these belong in principle the anions of the oxy-acids and halo-acids, although the name is not generally applied to these.

This does not always take place when in consequence of the incompleteness of the outermost shell belonging to the central atom the formation of a penetration complex might be possible, for in accepting bonding electrons from the groups into the outermost shell of the central atom, the number of electrons obtained does not always correspond to a stable shell. But sometimes penetration complexes occur even when this condition is not fulfilled, although their formation frequently fails to take place. Thus the aquo-complex of divalent cobalt $[\text{Co}(\text{OH}_2)_6]^{2+}$, which so easily loses its water of crystallization, is *not* to be reckoned among the penetration complexes. The incompleteness of the outermost shell of the cobaltous ion with its 7 electrons remains, although by taking up 12 electrons the structure of the krypton atom can *nearly* be achieved.

It is not always so easily decided from the chemical behaviour whether a penetration complex occurs or not, as in the case of the hexammine-cobaltic ion $[\text{Co}(\text{NH}_3)_6]^{3+}$ or that of the hexaquo-cobaltous ion $[\text{Co}(\text{OH}_2)_6]^{2+}$. Often a special investigation is necessary with the help of physical methods which furnish the information whether and how far a shell is filled. Even when the matter appears to be clear from the chemical behaviour, such investigations provide a desirable confirmation along completely independent lines. *Magnetic investigations* have proved themselves especially valuable for answering questions regarding the activity of the valence electrons effecting the bonding of the atoms within complexes (Chapter V, p. 396 ff).

The following may be cited as examples of complexes which are known with certainty to be penetration complexes, in addition to the complexes of trivalent cobalt already mentioned^{17a}:

The anion of chloroplatinic acid PtCl_6^{2-} , to be thought of as formed from Pt^{4+} and 6Cl^- .

Pt^{4+} possesses 6 electrons in its outer shell. Adding to this the 12 bonding electrons of 6Cl^- makes 18, which, when subdivided into $10 + 8$, gives the outer shell of the rare gas radon.

Alternatively, Pt with atomic number 78 possesses 78 electrons. To these are added 6 valence electrons from the Cl atoms and the 2 electrons stipulated by the negative charge of the complex which makes 86 (= the

¹⁷ The expression was chosen because with such complexes the volume occupied by the complex ion is considerably smaller than the volume of the components from which it is constructed, that is, a certain degree of penetration by the latter occurs.

^{17a} Stable shells in complexes: R. GILCHRIST, *Chem. Rev.*, 1943, **32**, 349 ff.

number of electrons of the rare gas radon, whose atomic number is 86).

The anion of ferrocyanic acid $\text{Fe}(\text{CN})_6^{4-}$ is to be thought of as formed from Fe^{2-} (= 6 outer electrons) and 6CN^- (= 12 bonding electrons), which together make 18 (= 10 + 8, corresponding to the rare-gas shell of krypton).

The anion of octacyanotungstic acid $\text{W}(\text{CN})_8^{4-}$: tungsten has 74 electrons, the 8 negative monovalent cyano groups supply 8 bonding electrons, to which 4 are added for the negative charge on the complex. Altogether $74 + 8 + 4 = 86$, the number of electrons of the rare gas radon.

As these examples show, the calculation whether or not the formation of a penetration complex should lead to a stable outer shell for the central atom can be undertaken in two ways. The complex is either thought of as being built up of ions — in the same way as when the charge is schematically calculated — or the electrons of the central atom are summed up with the bonding electrons contributed by the groups and the number of charges on the complex. In the case of cations the number of positive charges has to be subtracted from the total number of electrons, whereas with anions the number of negative charges must be added.

Not all penetration complexes fulfil the condition that a fully completed outer shell be attained by the central atom, as in the examples given here. Thus the really stable aquo- and ammine-complexes of trivalent chromium are certainly to be reckoned among the penetration complexes, although the number of electrons in them attains only to the element arsenic — atomic number 33, electrons in the outer shell $2 + 3$ — which is not distinguished by any special stability of its outer shell. Yet in the case of trivalent chromium, the co-ordination number 6 is met with in its aquo-, ammine-, acido- and mixed complexes just as constantly as in the case of trivalent cobalt. A further example is the anion of ferricyanic acid $\text{Fe}(\text{CN})_6^{3-}$, to be compared with the anion of ferrocyanic acid $\text{Fe}(\text{CN})_6^{4-}$.

Thus, if the number of valence electrons surrounding the central atom in a penetration complex does not exclusively fix the co-ordination number, on which symmetry factors also exert an influence as far as the arrangement of the groups is concerned, it is certain that under certain circumstances it can turn the scale against the symmetry factors, or is able at least to influence the symmetry relationships; for the symmetry of the group arrangement, although frequently, is by no means always the highest imaginable (pp. 110, 134). It is noteworthy that in the especially stable penetration complex $\text{Mo}(\text{CN})_8^{4-}$ containing a xenon shell, the eight cyano groups do not lie at the corners of a cube but are situated at the corners of a dodecahedron with eight apexes and triangular sides¹⁸.

¹⁸ J. L. HOARD and H. H. NORDSIECK, *J. Am. Chem. Soc.*, 1939, **61**, 2853. Chapter III, p. 134.

(iii) Differences in Structural Viewpoints concerning Inorganic and Organic Compounds

The systematization of inorganic compounds, as given by the co-ordination theory, commences with the consideration of a single atom around which are arranged other atoms whose arrangement relative to the first atom is a main consideration. In again utilizing these atoms in suitable cases as the starting-point of a new but similar way of thinking, not only can compounds of the second order be fitted into the scheme, but also those of still higher order, from the polynuclear compounds to the crystal lattices. The question how the atoms are held together, or, in other words, their *kind* of bonding, is relevant for electrolytically dissociable compounds only in so far as the ions as determined by electrolytic dissociation are recognized as structural units between which an *ionizable link* or, as is also said, an *ionic bond* exists. This division into cation and anion is, it is true, of unusual importance for the correct execution of the systematization and simplifies it considerably. Where it is not directly possible, as with the silicates, additional aids are required in order to accomplish a correspondingly useful study. The kind of bonding between the atoms within a complex does not at first need to be questioned. It suffices to accept these as given by experiment as in the case of the co-ordination numbers. Naturally, one will not be satisfied in the long run with this angle on the subject, but will try to penetrate deeper into the structures of the complexes.

The structural views of the co-ordination theory which lead to a systematization thus proceed in the first place from a spatial description. The enquiry into the kind of interaction between the atoms leading to bonding occurs, apart from the case of an ionizable link, only in the second place. This procedure for the framing of a systematization in inorganic chemistry is just the reverse of that in organic chemistry where one begins with atomic linking represented by a joining-line between two atoms that can also be doubled or tripled if necessary. The question of the spatial structure in organic chemistry takes only second place. It is well-known that the stereochemical ideas were not easy to put over. Indeed, there was actually a measure of hesitation in transferring the formulae from the plane of the paper into three-dimensional space, even when stereochemistry was by no means rejected¹⁹. The reason for this is to be sought in the fact that chain structures predominated with the compounds first investigated, and that the form of such a chain molecule is not unequivocally fixed by virtue of representation as a model, nor is it to be experimentally fixed without the assistance of new kinds of physical aids. (Certain criteria, like, for example, ring-closure reactions with substituted dicarboxylic acids, will be disregarded here.) In many

¹⁹ See, for example, P. DUDEN and M. SCHARFF, *Liebigs Ann. Chem.*, 1895, 288, 218. In the case of hexamethylenetetramine they state: "The suggested formula possesses the unusual feature that it can be constructed undistorted in model form only in space."

cases it is sufficient to know which atoms are directly linked to each other in order to be able to deduce their reactions. In inorganic chemistry, on the other hand, the question of the spatial structure for predominantly crystalline substances, which frequently remain in the crystalline state at high temperatures, is the more urgent one. The extension of the co-ordination theory to crystals, where it later proved to be capable of further development, was undertaken firstly by PFEIFFER²⁰ and shortly afterwards by NIGGLI²¹. It proved that the placing of this question in the forefront was justifiable. WERNER had not effected this to anything like the extent that could have eventuated. On the contrary, he proceeded originally from ideas concerning "valence", that is, concerning the linking of the atoms to one another. This is understandable in view of the predominance of such viewpoints in the period around 1890, and WERNER had to disentangle the consequences which resulted quite generally from the transference of ideas concerning valence from organic to inorganic chemistry, in order to be able to free himself from wrong conclusions. He did succeed in removing some of these errors, but, in spite of this reforming action, was not able to free himself completely from the old ideas of valence, which he himself did not find satisfying. The presentation of his theory of co-ordination in his book *Neuere Anschauungen auf dem Gebiete der anorganischen Chemie* suffered from this. The consequence was that these ideas only slowly fought their way through to universal recognition and were only later valued in their broad significance, as well as for a long time scarcely receiving a mention in text-books. In his work, WERNER had included along with his ideas about principal and subsidiary valence much which did not directly concern systematization, and indeed often weakened systematic lines of thought. But one must not overlook the fact that, in his attempts to disentangle these matters, we are here dealing with a struggle to delve deeper into the causes of complex-formation. To be sure, one would not today employ the imperfect theoretical tools which were at WERNER's disposal but make use of the knowledge of atomic and molecular structure which has been gained meanwhile.

The necessity of considering the state of bonding of the atoms when dealing with the structures of compounds of higher order follows immediately from the fact that acid radicals bound in complexes do not give the reactions of the corresponding acid anions. WERNER therefore differentiated between non-ionizable acido groups bound in the first sphere (of the central atom) and acid anions which ionize or are bound in the second sphere, of which chloro-pentammine cobaltic chloride $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ and dichloro-tetrammine cobaltic chloride $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ are examples, as directly expressed by their formulae. The conclusion that within the complex certain atoms effect bonding to the central atom follows from the fact that compounds and acido groups with two functional groupings can occupy two co-ordination

²⁰ P. PFEIFFER, *Z. anorg. Chem.*, 1915, **92**, 376.

²¹ P. NIGGLI, *Z. anorg. Chem.*, 1916, **94**, 207.

positions. For example, in the ethylenediamine-complexes the two amino groups assume the rôle of two ammonia molecules. From this it is to be concluded that the link between the central atom and the ammonia is effected by the nitrogen atom. Similarly, it follows for the links with acido groups, of which two can be replaced by oxalato and carbonato groups, that bonding occurs by means of an oxygen atom. Further isomerism occurs in compounds which contain isomerizable groups of atoms bound to the central atom. These are to be explained in the same way as the corresponding isomers in organic chemistry, where the same groups of atoms are bound to organic radicals. Thus there are nitro-pentammine-cobaltic salts with the ion $[\text{Co}(\text{NH}_3)_5\text{NO}_2]^{2+}$, which are yellow-brown, and yellowish-red nitrito-pentammine-cobaltic salts which contain the ion $[\text{Co}(\text{NH}_3)_5\text{ONO}]^{2+}$; also thiocyanato- and isothiocyanato-pentammine-complexes with the ions $[\text{Cr}(\text{NH}_3)_5\text{SCN}]^{2+}$ and $[\text{Co}(\text{NH}_3)_5\text{NCS}]^{2+}$. With the NO_2 grouping the bond can sometimes be effected by the nitrogen atom and on other occasions by an oxygen atom, with the thiocyanato grouping sometimes by the sulphur and sometimes by the nitrogen atom (for further, see Chapter III, p. 103 ff).

Thus, without doubt, we are here dealing with a bonding to the central atom that is closely related to the bonding of groups in organic compounds. This bond is effected by means of an electron pair which is common to the mutually bonded groups, that is, it differs from the ionic bond in which the partners, the ions, have no electrons in common, but only closed electron shells. How such different *kinds* of bonding arise is a matter which will now receive discussion in its context.

4. Valency and Bond Types

(i) The Valency of Ions

The chemical bond linking atoms comes into existence through interaction between the electrons of their outermost shells, that is, the *valence electrons*. These electrons are called valence electrons because they determine the number of *valencies*. These in turn govern the numerical ratios in which the atoms of the various elements combine to form compounds.

The connection between the valency and the electrical properties is given directly by FARADAY'S Law. The valency of an element is the ratio of atomic weight to electrochemical equivalent weight. The valency of compound ions can be correspondingly ascertained. A distinction must here be made between the *positive valency* of cations and the *negative valency*

²² Nitro-pentammine cobaltic chloride is prepared from the chloro-salt and sodium nitrite in solution strongly acidified with hydrochloric acid, and nitrito-pentammine cobaltic chloride from aquo-pentammine cobaltic chloride and sodium nitrite in weak hydrochloric acid solution.

of anions. The fact that the valency is always a small whole number is explained by the fact that electricity, like matter, is atomistic by nature. This conclusion was first drawn by HELMHOLTZ. On the formation of ions, atoms or groups of atoms either split off a small number of electrons, when cations result, or take up a small number of electrons to produce anions. Substances which result from the combination of ions must always contain these in a ratio such that their positive and negative charges compensate each other.

The valency of an element can often be inferred directly from its position in the Periodic System, or, better still, derived from the atomic structure. Difficulties occur when the element can have more than one valency, or when the number of valence electrons — which as the number of electrons in the outermost incomplete shell follows from the atomic structure — is not the unequivocal criterion for it, as, for example, in the case of iron. Apart from these by no means rare instances, the positive valency of an element is equal to its group number, which is the same as the number of valence electrons it must give up on the formation of an ion. The negative valency is equal to the difference between the group number and 8, which is the same thing as the number of electrons by which the outer shell is deficient from 8. The reason for this rule is that the atoms try to develop a specially stable complete shell as their outermost shell, which in turn can result by the losing or gaining of electrons. The octets as possessed by the rare gases are specially stable, and are therefore especially readily attained in ion-formation. Rather less stable are the shells of eighteen electrons, as found in the last elements of group VIII, that is, Ni, Pd and Pt, where the relinquishing of electrons on the formation of cations frequently stops. But anions do not occur in which a shell of 18 has been completed by the assumption of electrons.

For the derivation of valency from the atomic structure, the chemist can accept the special stability of the shells of 8 and 18 electrons as a fact, without enquiring further into its cause. The investigation of the cause demands in the last resort an explanation of the Periodic System on the basis of atomic structure, which can only be supplied through the most recent resources of physics. But such an explanation is finally needed in the cases where the rule given here for the derivation of valency fails. For these, not only is a knowledge needed of the way the electrons are combined into stable shells, but also of the subdivision into groups which has to be made within the shells, for example, the division of a shell of 18 into groups of $2 + 6 + 10$. But even this knowledge does not suffice in all cases to explain the valencies of the ions as determined in aqueous solution, for example the trivalence of chromium in the chromic ion. On the other hand, the division of the incomplete 18-shell into groups is sufficient to account for the divalence of manganese in the manganous ion (see Chapter X, 6, (ii)).

(ii) The Heteropolar Bond

In the saltlike compounds, chemical bonding between the atoms results in the transference of one or more valence electrons from one atom or group of atoms to another, so that ions with stable outer shells are formed. The cohesion of these ions can be described by means of the electrostatic forces of attraction, which act according to COULOMB'S Law. The structural units of the compounds, like atoms of the elements, form structures which consist of an atomic nucleus with an envelope containing a fixed number of electrons. They are distinguished from the atoms from which they are formed by the stability of their outer shells, and in this are characteristically different. For example, the sodium ion corresponds to the rare gas neon, the chloride ion to the rare gas argon. The fact that, in contrast to the rare gases, strong binding forces are active between the ions of the rare-gas type arises from their electrical charges. Compounds which are built up in this manner from ions are characterized as *heteropolar*, and the chemical bond between the atoms which is associated with them as the *heteropolar bond* or *ionic link* (pp. 37, 60).

The ions from which the heteropolar compounds are formed can be imagined as represented by rigid spheres — structures with the rare-gas configuration possess symmetry — which, in compound-formation, approach until they touch. This contact between the spheres does not, however, mean a contact between the outermost electron shells, since repulsive electronic forces must arise between these when they approach each other too closely. The radius of the sphere serving as model must thus be greater than the distance between the nucleus and outermost electron shell. This *ionic radius* can be derived from the distance between the centres of the ions in the lattice (Chapter VIII, 4, (i)).

With the assumption of rigid ions, a repulsive force between the electron envelopes must be added to the electrostatic attraction between the ions in order to maintain equilibrium with the attractive COULOMB force and result in a stable structure. It can be empirically deduced from the compressibility of heteropolar compounds that the approach of ions beyond their normal lattice distance is opposed by a force varying inversely with a high power of the separation.

The representation of ions by rigid spheres corresponds to the actual relationships to a certain approximation only. The stabler the electronic envelopes the closer this approximation, for it is to be expected that on the approach of the ions to the smallest permissible distance the electron envelopes do not remain completely unaffected. This fact is expressed here by the nature of the opposing forces in the representation selected for the maintenance of stable structural arrangements through the equilibrium of forces. These do not appear suddenly during the approach, as would of necessity be the case for complete rigidity, but in a degree depending upon

the distance. Here, admittedly, the law of force corresponds to a high power of the proximity, thus indicating that a "suddenness" is to some extent realized.

The ions with rare-gas shells correspond to the rigid, spherical model most satisfactorily. Those with 18-shells like, for instance, Ag^+ , do not correspond so well, nor do those with other outer shells, such as Fe^{2+} or Fe^{3+} . Hence, with such ions, one must reckon with a more or less strong *deformation of the electron envelope* in combination. The form this deformation takes and how it can be determined experimentally remains for the present undecided. It might be asserted, however, that compounds containing such ions, like AgCl , for example, are no longer strictly heteropolar, although they conduct electricity both in the fused state and in solution. These conclusions indicate that the *heteropolar bond* represents a *limiting case* which is only realizable to a greater or lesser approximation.

Without immediately investigating these limits within which the bond may be regarded as heteropolar, the attempt will be made to utilize this heteropolar conception as far as possible for explaining the construction of chemical compounds from their atoms. This attempt, like the representation of the heteropolar bond given until then, is due to KOSSEL, who in 1916 understood for the first time how to make the knowledge of atomic structure useful in explaining the chemical bond. It is noteworthy how he trod in the main in the footsteps of BERZELIUS, naturally avoiding the physical errors which BERZELIUS made. KOSSEL applied the electrochemical-dualistic theory consistently on the basis of the new knowledge, as far as this was at all possible (p. 36 ff).

So far, we have considered the binary separation of heteropolar compounds into ions which results on electrolytic dissociation. We can now go a step further with KOSSEL and carry out a corresponding dismemberment of the complete ions, including the ions of the oxy-acids. According to this, these also are in the last resort built up of ions, which, however, must be considerably more tightly bound to one another than the ions arising through dissociation in solution. Thus, for example, the SO_4^{2-} ion is built up from one sulphur ion with a valency of +6 surrounded by four oxide ions with a valency of -2; the ClO_4^- ion from Cl^{7+} and four O^{2-} , the PtCl_6^{2-} ion from Pt^{4+} and six Cl^- . The sulphur and chlorine respectively appear as electropositive towards oxygen, in just the same way as was supposed to occur in S^+O_3^- , assumed by BERZELIUS as a structural unit for the sulphates. The excess negative charge which BERZELIUS assigned to the SO_3 molecule, in order that it might bind the electropositive basic fragment K_2^+O^- , has become the charge on the combined ion SO_4^{2-} . This picture of the structure of complex ions has also been applied to the silicates for which the ions Si^{4+} , O^{2-} , Al^{3+} , etc. were assumed. Indeed it has been carried as far as calculating radii for these ions and employing spheres of definite radii as models for the hypothetical ions. In this the positive ions,

because the outer electrons of the corresponding atoms are lacking and the electron envelopes remaining underneath are subject to the action of a high positive nuclear charge (for example, +4 for Si, +6 for S, +7 for Cl), naturally turn out to be quite small in comparison with the negative ions.

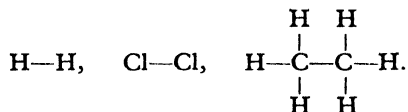
From many viewpoints, this picture is doubtless attractive on account of its simplicity, as well as being convenient. Yet one must not be misled into seeing in it a true representation of the bonding relationships²³. Further, in one important point it does not do justice to WERNER's co-ordination theory. Alone from experiments with the complex cobaltamines, WERNER deduced that there must be two types of chlorine bonds, the non-ionic and the ionic. If, for example, the chlorine within the complex $[\text{Co}(\text{NH}_3)_5\text{Cl}]^+$ is regarded afresh as bound like an ion, it is no longer understandable why it will not also split off like an ion in solution. From theoretical grounds, moreover, the gathering of normal ions about a central atom with a high positive charge is unlikely, for, as already pointed out, the ions are not rigid structures, their electron envelopes being deformable. Since the magnitude of the deformation depends, apart from the structures of the outermost electron shells, on the strength of the deforming power, which is quite considerable for central atoms with high positive charges, it follows that in ions such as SO_4^{2-} , ClO_4^- , PtCl_6^{2-} and in the silicates one is dealing with at least very strongly "deformed" O^{2-} or Cl^- ions respectively. Thus, not even an approximately pure heteropolar bond is under discussion. The heteropolar bond is simply, as already mentioned, an ideal limiting case which can be more or less distantly removed from reality. There are transitions which eventually lead to another limiting case, in which opposing polar charges no longer play a part since they are no longer extant.

(iii) The Homopolar Bond

This other limiting case is realized in those substances in which similar structural units are joined to each other, as are, for the sake of examples, the two hydrogen atoms in the hydrogen molecule H_2 , likewise the atoms in all other diatomic molecules of individual elements, and the carbon atoms in hydrocarbons such as $\text{H}_3\text{C}-\text{CH}_3$. This type of bond is named the *homopolar bond*, and the substances containing them, the non-electrolytes, are *homopolar* — unfortunately a less happily chosen expression. Here there are two, or on occasions more than two, electrons common to the two atoms known as bonding electrons which, in consequence of special interactions only to be understood in the light of the quantum theory, effect the bond. In the simplest case, such as exists in the hydrogen molecule, the chlorine molecule and the paraffinic hydrocarbons, there is one bonding electron *pair*,

²³ A. E. VAN ARKEL and J. H. DE BOER follow the principle depicted here to its ultimate consequences in their book: *Chemische Bindung als elektrostatische Erscheinung*. Their extreme viewpoint can today be regarded as completely overthrown.

to which each of the two atoms participating in the bond contributes one valence electron. It is symbolically represented by a joining-line. This had already long been in use as a symbol for the chemical bond before anything concrete like an electron pair could be seen in it. Thus the examples cited are written:



As many valence-lines radiate from each atom as electrons are contributed by it for bond-formation.

If the atom contributing electrons to the bond possesses more valence electrons than are operated in the chemical bond, these remain over. Since an even number is usually being dealt with — compounds with unpaired electrons are very rare — these are collected into pairs which are known as *lone electron pairs*. In the valence-line formulae they do not appear. If it is desired to give expression to them, they can be written on the respective atoms as pairs of dots or alternatively as transverse lines. Thus Cl—Cl can instead be more completely represented by $:\ddot{\text{Cl}}-\ddot{\text{Cl}}:$ or $|\overline{\text{Cl}}-\overline{\text{Cl}}|$.

The manner in which *valence-line formulae* are written down differs characteristically from that for the *co-ordination formulae*. In the latter the units which are known as ions are placed next to each other without a joining-line, or separated from each other respectively by square brackets: NaCl, $[\text{Co}(\text{NH}_3)_6]_2[\text{SO}_4]_3$, $\text{K}_4[\text{Fe}(\text{CN})_6]$. This difference in style has a deeper meaning. The structural units separated from each other by brackets face each other as structures with closed electron shells. These do not make contact with their outer electron clouds, so that an empty space, that is, one not filled with electrons, remains between them. The atoms joined by lines in the valence-line formulae, on the contrary, are actually held together by the electrons situated between them. This difference appearing in the symbolism receives direct support by experiment (see later).

(iv) Molecular Dipoles

An equal sharing of the bonding electrons between the two atoms of a homopolar bond occurs only if these atoms are identical. Otherwise the dissymmetry of the structure with respect to the atomic nuclei causes an additional dissymmetry in the distribution of the electrons, whereby the centre of gravity of the positive charges relative to that of the negative charges becomes displaced in the direction of one of the atoms, and a dipole is formed. A molecule with a clearly recognizable polarity results without altering the essential character of the homopolar bond. The direction of the displacement of charge can frequently be derived from the known electron

affinities of the elements. Thus, in chlorine iodide the iodine forms the positive and the chlorine the negative pole: $\text{Cl}^- - ^+\text{I}$. In methyl chloride $\text{H}_3\text{C}^+ - ^-\text{Cl}$, the chlorine similarly forms the negative pole. The magnitude of the charge displacement is measured by the *dipole moment* μ , this being the product of the charges thought of as collected in the centres of gravity and the distance between these charge centres²⁴. This product has an order of magnitude of 10^{-18} e.s.u. \times cm ($= \text{g}^{1/2}\text{cm}^{3/2}\text{sec}^{-1}$) $=$ 1 Debye $=$ 1 D, which follows from the order of magnitude of the interatomic distance, 10^{-8} cm, and that of the unit electronic charge, 4.8×10^{-10} e.s.u. The larger the dipole moment, the further removed is the bond between the atoms from that of pure homopolar character and the nearer it is to the state of a heteropolar bond. If the centre of gravity of the positive charges coincides with the nucleus of one atom and that of the negative charges with the nucleus of the other atom, then ions result and the transition to a strictly heteropolar bond is complete.

As an example of a molecular dipole, in which it can be clearly recognized how far it is removed from the extreme case of the heteropolar bond, *hydrogen chloride* might be mentioned. Its dipole moment is $\mu = 1.08$ D. The distance between the hydrogen and chlorine nuclei is 1.27×10^{-8} cm²⁵. If hydrogen chloride were heteropolar, a stripped hydrogen nucleus and a chloride ion would face each other, so that the moment of such a molecule, in which the unit charges $+e$ and $-e$ are at a separation of 1.27×10^{-8} cm, would possess the value 4.8×10^{-10} e.s.u. \times 1.27×10^{-8} cm or ~ 6 D. In reality, however, it is only one sixth of this. Thus, in hydrogen chloride, the state of bonding is very far removed from the heteropolar type. From the smallness of the moment, it must further be concluded that the valence electrons of the hydrogen and the chlorine atoms are, to a high degree, common to both atoms. Hydrogen chloride is thus to be reckoned among the homopolar compounds. The correctness of this assumption is confirmed by the structure of crystalline hydrogen chloride among other things. The contradiction of this conception by the fact that in aqueous solution hydrogen chloride is practically completely dissociated electrolytically is only apparent. Thus the ions which it forms in aqueous solution are not simply H^+ and Cl^- , as usually written for the sake of simplicity, but the hydrogen ion is in reality the hydrated proton, the *hydroxonium ion*: $\text{H}^+ + \text{H}_2\text{O} = \text{H}_3\text{O}^+$ ^{25a}.

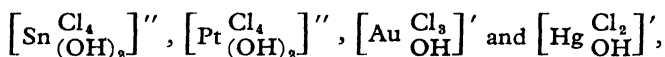
Similarly to the manner in which hydrogen chloride must be conceived as an essentially homopolar compound possessing polar character, there are numerous other compounds which can be thought of as built up of ions, but in their state of bonding are essentially nearer to homopolar than to heteropolar bonding. It is true that unambiguous experimental evidence concerning this point is not always to hand, such as is in the case of hydrogen

²⁴ Concerning the measurement of dipole moments, see Chapter V, p. 339 ff.

²⁵ Concerning the estimation of this value, see Chapter V, p. 358.

^{25a} A. R. HANTZSCH was the first to recognize this.

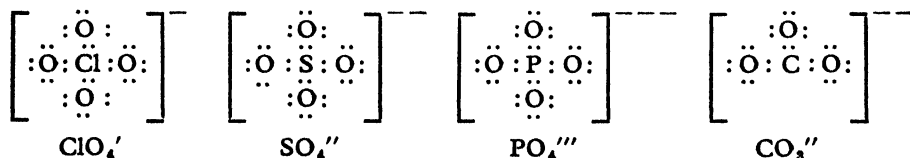
chloride. Where this is lacking, compounds of the first order, at least, which in aqueous solution form none of the ions corresponding to their composition, may be viewed as essentially homopolar. For example, SnCl_4 , PtCl_4 , AuCl_3 and HgCl_2 form none of the elementary cations Sn^{\cdots} , Pt^{\cdots} , Au^{\cdots} , Hg^{\cdots} ²⁶ in aqueous solution, but react instead with the water giving hydroxo-anions



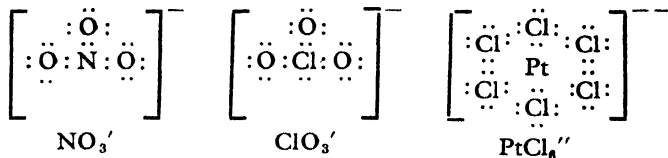
that is, compounds of higher order. But even when the ions corresponding to electrolytic dissociation arise in aqueous solution, the anhydrous compounds may not be spoken of with certainty as relatively strictly heteropolar, for, as with hydrogen chloride, the formation of hydrated ions — that is, again compounds of higher order — may play a decisive part. This is the case with AlCl_3 , which is to be conceived as an essentially homopolar compound, although with much water it splits up into the ions Al^{\cdots} and 3Cl^{\cdots} (admittedly with a simultaneous partial hydrolysis). The cation is here in reality the hexaquo-aluminium ion $[\text{Al}(\text{OH})_6]^{\cdots}$. Special investigations are thus frequently necessary in order to obtain any decision regarding the state of bonding by experimental methods independent of the process of electrolytic dissociation.

(v) Bonding in Complexes

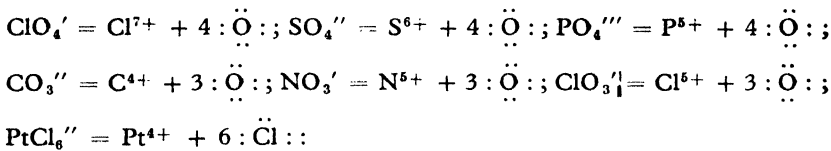
Transitions between homopolar and heteropolar bonding, as here portrayed for compounds of the first order, are met with again within the complexes of compounds of higher order. As already stated, the purely heteropolar models which can be constructed for these bonds by assembling oppositely charged ions are not appropriate, even though they correctly indicate the opposing charges between the central atom and the groups. If, however, a transition type between the two kinds of bonds should occur here, there must be an electron pair available which provides for the bond between the central atom and the group. The simplest case would be that each group were bound to the central atom by an electron pair. That there are such electron pairs effecting the bonds can in most cases be gathered without any difficulty from the valence electrons of the central atom and of the groups. If all the valence electrons are represented as dots, the following formula diagrams result:



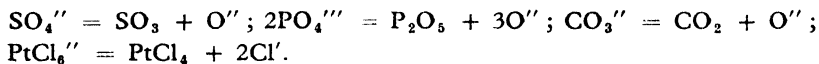
²⁶ Hg^{\cdots} is nevertheless to be assumed present in detectable quantity in a solution of HgCl_2 , in addition to $\left[\text{Hg} \begin{array}{c} \text{Cl}_2 \\ \text{OH} \end{array} \right]'$.



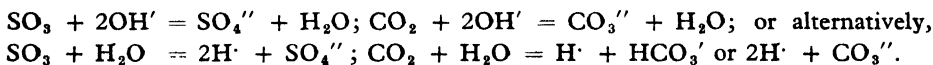
These complex ions can in each case be considered as arising either from the coalition of the central atom, more or less completely robbed of its shells of valence electrons, with the associated atoms or groups surrounded by completed octets, or, alternatively, by the approach of one or more ions to the central atom of a compound of the first order. Thus, for example, either



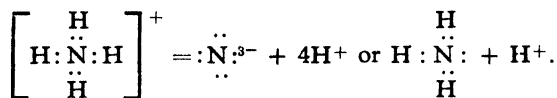
or else



The latter manner of formation corresponds to the formation of ions in aqueous solution, in which for the anions of the oxy-acids the reactions can also be formulated with hydroxyl ions. For example,

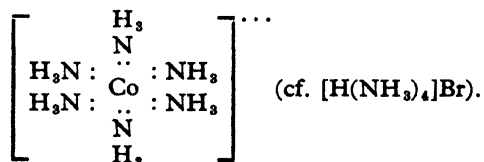


In a precisely corresponding manner, the ammonium ion can be thought of as formed either from N^{3-} and 4H^+ or by the approach of H^+ to the NH_3 molecule:



Again here the second formulation corresponds to the manner of formation in aqueous solution.

The bond between ammonia and the central atom in the complex amines can be formulated analogously to this manner of formation for the ammonium ion. Instead of the proton H^+ is inserted the metal cation robbed wholly or partly of its outer shell. In the resulting complex, the metal and not the nitrogen appears as the central atom, because several NH_3 molecules are attached to it:



Along these lines there is a further analogy to the ammonium compounds, since anomalous ammonium salts²⁷ exist in which a hydrogen atom is appropriately regarded as the central atom²⁸.

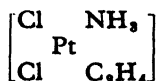
Just as the lone electron pair on the nitrogen binds ammonia, so can a like pair on the oxygen bind water to the central atom in the aquo-complexes. With a formulation of this kind, the demand implied by experiment that a definite atom of the molecule bound in the complex be linked to the central atom is fulfilled (p. 61).

In the complexes in which molecules and atoms or groups of atoms that otherwise appear as independent ions are linked side by side, these, irrespective of their different chemical natures, partake in the same kind of linking with the central atom, namely *bonding by an electron pair*. It depends upon the nature of the group (and also upon that of the central atom) whether the bonding electrons distribute themselves fairly equally between the central atom and the attached atom or whether they are more or less strongly drawn towards one of the two, in other words, how strongly polar the bond is. If the attached group is a molecule like NH_3 or H_2O , a slight shift of the lone pair of electrons towards the central atom means only a negligible "deformation", and hence a considerable degree of independence of the molecule bound in the complex. The water of crystallization in salts is bound in aquo-complexes. In salts which easily lose this, or, in other words, in salts containing water of crystallization with a high partial pressure of water vapour, a state of bonding of this kind is to be assumed for the water.

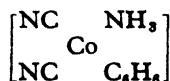
In the limiting case, where the molecule bound in the complex may be regarded as undeformed, the kind of bonding can be described as electrostatic, like the bond assumed between ions. As in the latter case, where two oppositely charged particles are attracted to one another, in the case charged end of the dipole, thus: $(+) \cdots (-)$. Hence a positively charged metal ion would attract a water molecule by its negative end, the oxygen, and an ammonia molecule by the nitrogen. How far in any given instance such a limiting case can be realized, still requires special investigation.

of a bond with a molecular dipole the central atom attracts the oppositely

That dipolar attraction alone cannot explain the bonding of a molecule in a complex follows from the fact that molecules which possess no dipole moment can also be bound in a complex, like, for example, ethylene or benzene.



dichloro-ammine-ethylene
platinum



dicyano-ammine-benzene
cobalt

²⁷ Review: A. WERNER, *Ber.*, 1903, **36**, 147 ff.

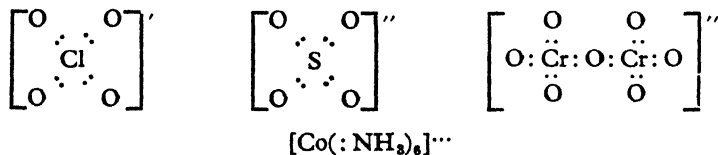
²⁸ Whether this formulation in which hydrogen attains the co-ordination number 4 is correct, is still open to doubt.

These examples show, however, that success cannot always be achieved with the assumption that an electron pair effects the bond between the central atom and an attached group. With ethylene and other olefines and diolefines²⁹ one could indeed utilize one pair of electrons from the double bond. However, it is questionable whether this is permissible³⁰. With complexly bound benzene, on the other hand, the drawing forth of two electrons from its bonding system is not admissible. The nature of complex formation still cannot be esteemed as understood in all cases.

(vi) Valency and Type of Bonding in Homopolar Compounds

The recognition of the structure of compounds of higher order, like the accomplishment of a useful systematization, has been rendered more difficult and delayed by the fact that two different kinds of bonding are to be assumed in these compounds, namely heteropolar and homopolar. To this must be added the fact that homopolar bonding by means of an electron pair can be brought about in different ways. Either one electron is contributed by each of the atoms taking part in the bond, or one atom supplies both bonding electrons. Whichever way the bond is brought about, the activity of the valence electrons within the compound is not affected. Thus the C—H bonds in CH₄ are similar in nature to the N—H bonds in NH₄⁺, although in methane one electron in each electron pair originates from the carbon and one from the hydrogen, while in the ammonium ion one proton is bound by the lone electron pair on the nitrogen of NH₃. In the completed complex NH₄⁺, none of the N—H bonds is different from the others.

It would therefore have been very simple for the symbolism to have employed one and the same symbol for each electron-pair bond. If each valence electron is represented by a dot, the system which G. N. LEWIS and I. LANGMUIR introduced for the illustration of the electronic theory of valency is attained; for example (cf. p. 37):



The non-utilized valence-electron pairs of the attached groups can also be added at will as pairs of dots or transverse lines if it is desired simultaneously to express the validity of the octet rule for each atom³¹.

Owing to the numerous dots, however, this system is not always very

²⁹ Review: R. N. KELLER, *Chem. Rev.*, 1941, 28, 229.

³⁰ W. HÜCKEL, *Theoretische Grundlagen der organischen Chemie* I, p. 113 (6th Ed., 1949).

³¹ B. EISTERT, *Ber.*, 1938, 71, 237. Cf. P. BAUMGARTEN, *ibid.*, 1937, 70, 2500. R. ROBINSON employs instead of the transverse lines short lines radiating from the atom: *Ahrens Sammlung chem. u. chem.-techn. Vorträge*, New Series, No. 14, p. 9.

clear. Moreover, from many points of view it has the disadvantage that the valencies of the elements bound in the complex are not indicated at the first glance. This can of course be read from the formula by counting up the electrons and the charge on the complex.

The desire to simplify the symbolism, as well as to include in it a clear representation of the valencies of the elements, led to considerable difficulties. These difficulties assumed a greater importance than they deserved when regarded from the standpoint of today. However, a closer investigation of them must not be omitted, since we are dealing here with the general problem of making the chemical formula useful for the systematization of chemical compounds in inorganic as well as in organic chemistry. The difficulties occurred because the electronic theory of valency thus far depicted had not been the starting-point for the derivation of chemical formulae. Rather, the derivation was one that had been attempted from different viewpoints. In point of fact, a symbolism was already in existence prior to the LEWIS-LANGMUIR electronic representation for homopolar compounds, namely the valence-line formula of organic chemistry, which frequently, but by no means in every case, permitted an effortless translation into the LEWIS-LANGMUIR symbolism. With this it is fitting next to consider the compounds of the first order.

In the year 1858, ARCHIBALD SCOTT COUPER created the symbol of the valence-line to illustrate the linking of carbon atoms and other atoms in organic compounds which he and KEKULÉ had recognized simultaneously. This indicates which atoms are directly linked with each other. These bonds, as we now know, are homopolar in nature and in the simplest cases effected by two electrons. For the bond linking two carbon atoms to one another, each atom contributes one electron, exactly as for the bond between the hydrogen atoms in the H_2 molecule or the chlorine atoms in the Cl_2 molecule. COUPER's *valence-line* is thus, from the modern standpoint, the symbol for the *electron pair*. From the structural formulae written with its help, it is moreover possible to read off the number of valence electrons contributed by each atom, this being equal to the number of valence-lines radiating from each atomic symbol as long as there is fulfilment of the condition that each of the two bonded atoms contribute one electron to the electron-pair bond. The two ends of the line indicate whence the electrons originate.

It is otherwise if *one* atom provides both the bonding electrons. This eventuality was not foreseen in the classical theory of valence, for the linking of two atoms was thought to be brought about by a kind of hooking process in which each atom operated one or more "hooks" firmly attached to it. The number of supposed hooks which an atom possessed or operated was equal to its valency. The hooks remained anchored to the atom after the formation of the bond, of which the symbolical representation used by KEKULÉ, later to be replaced by COUPER's valence-lines, bore witness. For each hook,

there had thus to be a counterpart present on the partner. This forced interpretation was no longer necessary as soon as it was recognized that electrons detachable from the atom were the cause of the bond. The example of heteropolar compounds shows that one or more electrons can completely change over from one atom to another. If ions with closed electron shells face each other, they are no longer held together by "hooks".

Under certain conditions, however, the ionic representation can be readily derived from the valence-line representation, that is, *provided the atoms are monovalent*, the relation between symbolism and the concept of valency appearing simultaneously. Hence the concept of *valency in homopolar compounds*, as originally defined in organic chemistry, will be discussed next.

By the *valency* of an atom, one here understands the *number of monovalent atoms* it is able to bind. If the atom is linked with other atoms which are polyvalent, the valency is only to be derived from such compounds under special suppositions. The concept of valence is thus not affected by the opposing polarity of the electrochemical valence concept derived from FARADAY'S Law. Whether, in deriving the valency, the compounds of a particular element with the electronegative chlorine or fluorine on the one hand or with the electropositive hydrogen on the other are considered, is in principle immaterial. However, it can happen that the atom exhibits different valencies towards halogens and towards hydrogen. An example is sulphur, which is tetravalent towards fluorine in SF_4 and hexavalent in SF_6 , but divalent towards hydrogen in H_2S . But this is not always so, nitrogen being trivalent in NF_3 and NCl_3 , as also in NH_3 ; whereas a similar constancy in valency is universally valid for carbon where — apart from a vanishingly small number of exceptions — it is equal to 4.

There are thus two definitions of valency, one for heteropolar and one for homopolar compounds. The different definitions of the same concept have a historical foundation. In the first place, the concept of valence was derived from the composition of homopolar carbon compounds like CH_4 , CCl_4 , $N(CH_3)_3$, $O(CH_3)_2$, $As(CH_3)_3$, $Zn(CH_3)_2$, $Hg(CH_3)_2$, etc. To be sure, other expressions were at first used for it, such as saturation capacity of the atoms, or atomicity. This derivation occurred at the same time as the recognition of the principle of atomic chains in carbon compounds and the introduction of correct atomic weights. Had the latter been accomplished earlier, which would have been quite possible, then the relation between equivalent weight and atomic weight, fixed unambiguously by FARADAY'S Law discovered in 1834, would have led first to the electrochemical definition of valence with opposite polarities.

It is questionable whether the two definitions of the valence concept are compatible with each other, and to what extent. The fact that until now each has held its ground in the presence of the other surely indicates that the affirmative must be the case, at least to a certain point.

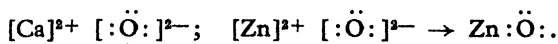
The relationship is clearest for monovalent atoms where it can also be illustrated with the help of formula symbolism. For homopolar bonds, the atoms are joined by a valence-line, which is equivalent to an electron pair. If the two atoms are the same, the electron pair belongs equally to both, and on the average one valence electron is apportioned to each atom. If they are dissimilar, as in hydrogen chloride, the electron pair is drawn over towards one atom which then forms the negative end of the molecular dipole: $\text{H}^+ \text{---} \text{Cl}^-$. According to the nature of the bonded atoms, the polarity of the bond can assume all possible degrees until, in the extreme case, the electron pair has completely slipped over to the electronegative element; or until, so to speak, the valence-line has crept completely into the symbol for the electronegative atom. As soon as the polarity of a bond is fixed, a formal analysis of the compound into a positive and a negative ion can be undertaken, and the electropositive valency of one atom and the electronegative valency of the other spoken of. Such an analysis can also be carried out when a polyvalent atom unites itself to several identical monovalent atoms. In many cases the direction of the polarity of a bond can be derived by analogy, while in others special experiments will be necessary to determine this. A decision may frequently be extraordinarily difficult. Thus there will be no doubt that hydrogen is to be designated as electropositively univalent in HCl and H_2O . On passing to NH_3 , a more thorough reflection is necessary, whereas with CH_4 one might be completely in doubt whether the C—H bond were polar in the sense $\text{C}^- \text{---}^+ \text{H}$ or in the sense $\text{C}^+ \text{---}^- \text{H}$ ³². The sulphur in SF_6 and SF_4 may be regarded without doubt as electropositively hexa- and tetravalent in the sense of an analysis into $\text{S}^{6+} + 6\text{F}^-$ and $\text{S}^{4+} + 4\text{F}^-$, although in reality a disruption of SF_6 and SF_4 into ions never occurs.

For compounds in which bonds between dissimilar atoms possess a dipolar character, the homopolar concept of valence can in this manner be extended in the direction of opposing polarity, and in so doing assimilate the heteropolar concept of valence. The valence number is the same in the two cases. A prerequisite for this agreement is that the atom, whose valency is to be defined, be linked with one or more *similar monovalent* atoms. As soon as the requirements of *monovalence* and of *similarity* of the bound atoms are not fulfilled, agreement is not always to be obtained between the two definitions of valence, and the derivation of a separate heteropolar or homopolar formula symbolism is sometimes impossible.

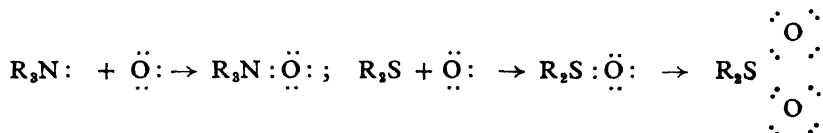
For calcium oxide, which very closely approaches the extreme case of the heteropolar bond, the two valence electrons of the calcium enter into

³² Concerning the polarity of the C—H bond, see C. A. COULSON, *Trans. Faraday Soc.*, 1942, **38**, 433; A. D. WALSH, *ibid.*, 1947, **43**, 60; *Discussions Faraday Soc.*, 1947, **2**, 18; *J. Chem. Soc.*, 1948, p. 398; H. KEMPTER and R. MECKE, *Z. Naturforsch.*, 1947, **2a**, 549; C. N. HINSHLWOOD, *J. Chem. Soc.*, 1948, p. 531; R. P. BELL, H. W. THOMPSON and E. E. VAGO, *Proc. Roy. Soc.*, 1948, **A 192**, 498; W. L. G. GENT, *Quart. Rev. Chem. Soc.*, 1948, **2**, 383 (review).

the gap in the oxygen octet. The transition to a more homopolar bond would have to be represented by the attraction of this electron pair towards the cation:

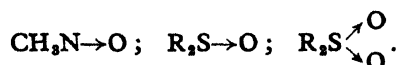


The less stable the outer shell of the cation, the more this shift will occur. Thus for calcium with its shell of 8 electrons it will almost fail to appear, while for zinc with its shell of 18 it is already noticeable. The two atoms will hold the electrons still more in common if the detaching of the two electrons from the positive partner on complete ionization would create a gap in its stable outer shell. This is the case where a lone electron pair effects the bonding to an oxygen atom, as with the amine oxides, sulphoxides and sulphones:



This kind of homopolar link is named a *semi-polar bond*. It is an electron-pair bond like the usual homopolar bond. It is always polar in the sense that the atom supplying the electrons is the positive and the atom accepting them for the completion of its shell the negative end of the dipole. The link is termed semi-polar because, in an idealized case in which the two bonding electrons were equally shared between both atoms, the atom supplying the electrons would bear exactly one positive and the other atom exactly one negative unit of charge as excess charge. Experience shows that an extremely high charging of this kind, which is exactly intermediate between uncharged atoms and doubly charged ions, is never achieved for decidedly homopolar compounds of the types instanced above, for the dipole moments of these compounds are markedly smaller than would correspond to such a distribution of charge. For an interatomic distance of 1.2 Å, the moment of such a bond would have to amount to about 5.8 D.

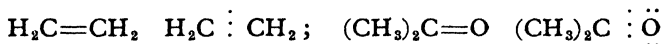
The symbol for the semi-polar bond in the LEWIS-LANGMUIR symbolism is a pair of dots, that is, precisely the same as for an ordinary homopolar bond. If this symbolism is to be translated into the valence-line representation holding fast to the dash as denoting two electrons, the two atoms participating in the semi-polar bond must be joined by a single line exactly as for a simple homopolar bond. With the semi-polar bond, however, in order to denote that one atom is the donor and the other the acceptor of the electron pair, it has been agreed to distinguish the direction of the donation of the electrons by an arrow-head on the valence-line, thus:



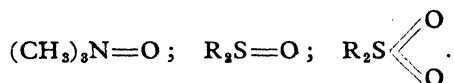
But in this symbolism, the connection between the valence-line representation and the valency, which exists for bonding with monovalent atoms,

is lost. The total number of electrons operated by the atom yielding up its electrons, and thereby its valency, cannot be read off directly from the formula by the number of valence-lines radiating from the atom, nor likewise by the number of electrons taken up by the other atom.

The connection remains, however, if the valence-line symbolism is written as was usual before there was any knowledge of the physical meaning of the valence-dash. Formerly the formulae were constructed so that each atom received as many valence-lines (hooks) as corresponded to its valency, these lines (hooks) having to fit in with one another. This was possible without further ado for polyvalent atoms, if one wrote *double bonds*. Translated into the language of the electronic theory, such a double bond means the operation of two electron pairs, and in the LEWIS-LANGMUIR symbolism is in consequence to be replaced by four dots; for example:



Double bonds of this sort were also written where, according to modern ideas, a semi-polar bond, that is, a bond involving one electron pair occurs:



From these formulae the valency of the corresponding atoms can be read off, being equal to the number of electrons respectively operated by the nitrogen and sulphur and required by the oxygen. Thus this principle of formulation indubitably had a considerable constructive value, since it always allowed the linking up of the correct number of atoms on the basis of the principle of atomic chains and the valency of the individual atoms towards one another. It has therefore been used up to the present time as the basis of formula-derivation in organic chemistry.

Nevertheless, it began to be realized, very much on the late side it is true, that not all examples written as double bonds were similar in their chemical behaviour. For the unsaturated hydrocarbons and the carbonyl compounds, it was usual to connect the symbol for the double bond with an additive power of the atoms so bound, these tending to break up the double bond with the formation of a single bond. Yet this was totally out of the question for amine oxides, sulfoxides and sulphones, whereas for nitro-com-

pounds, in which the nitro group was written $-\text{N} \begin{array}{l} \diagup \text{O} \\ \diagdown \text{O} \end{array}$, this was only the

case to a very slight extent. We now know that this difference is conditioned by the fact that these compounds do not contain double bonds consisting of two electron pairs, but semi-polar bonds. Double bonds with additive powers, however, are bonds which are indeed effected by two electron pairs. Of these, one behaves itself differently from that effecting a single homopolar bond and brings about the addition reactions. Only for such double bonds is it permissible to translate the two dashes directly into the language of the

electronic theory by means of the rule that 1 valence-line = 2 electrons.

If one wishes to write correctly the formula of a compound in which a polyvalent element contributes more than one electron to a bond, the chemical behaviour of this bond must be known. But there are two additional rules according to which one may be guided in most cases, even when the chemical behaviour is not known. Firstly, a true double bond is possible as a rule only between elements of the first period. Secondly, each atom tries in general to surround itself with 8 electrons (the octet rule), 8 being in any case the highest possible number for elements of the first period. With the help of these rules, the classical formulae containing double bonds can easily be "corrected" where necessary. To be sure, an entirely satisfactory formulation is not always attained if in any given case a semi-polar bond is written in place of the double bond, in particular where mesomerism (p. 424 ff) exists. But such cases need not be considered here.

5. Valency and State of Bonding in Compounds of Higher Order

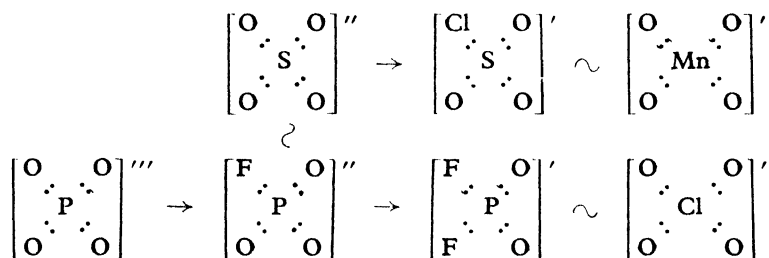
The considerations which have been introduced for compounds of the first order are also valid for compounds of higher order. In order that these may be formed from compounds of the first order, the latter must fulfil certain constitutional conditions, a prerequisite being the presence of a lone electron pair on the one part and the existence of an incomplete shell on the other. The latter condition is not always essential, namely when the lone electron pairs can form a reasonable stable shell on their own, rather like the aquo-ions $[\text{Mg}(\text{OH}_2)_6]^{2+}$ and $[\text{Ca}(\text{OH}_2)_6]^{2+}$. Since in these cases the kind of activity of the lone electron pairs appears scarcely to be altered with respect to the isolated compound of the first order, and since there are transitions between more or less firm inclusions into other shells, it is thus not fitting to speak of changes in valency of the atoms with the formation of compounds of higher order from compounds of the first order. The following rule is thus valid:

The valency does not change with the formation of compounds of higher order.

Nitrogen in sal ammoniac $[\text{NH}_4]\text{Cl}$ is thus trivalent as in ammonia, sulphur in the sulphates hexavalent as in sulphur trioxide, platinum in chloroplatinic acid tetravalent as in PtCl_4 . The same conclusion is also arrived at if the complexes in the compounds of higher order are schematically thought of as split up into ions: $[\text{NH}_4]^+$ into $\text{N}^{3+} + 4\text{H}^+$, $[\text{SO}_4]^{2-}$ into $\text{S}^{6+} + 4\text{O}^{2-}$, $[\text{PtCl}_6]^{2-}$ into $\text{Pt}^{4+} + 6\text{Cl}^-$.

The electron-pair bonds within the complexes come into existence exactly as for compounds of the first order, either by each partner contributing one electron, or by one partner supplying both electrons. The former case occurs when a monovalent atom and the latter when a divalent atom is linked to a central atom with an incomplete shell. In the sense of the differentiation

met with in compounds of the first order, a single bond would exist in the one case and a semi-polar bond in the other. Yet this differentiation is here only formal, because the single bond, since we are dealing with a link between two different atoms, is here always more or less strongly polar and possesses a dipole, as does also the semi-polar bond. The degree in which the bonding electrons of the central atom are drawn over towards the group in question varies according to its nature. It is well within the bounds of possibility that the dipole moment of the bond of a monovalent atom is about as large as that of the semi-polar bond of a divalent atom. Indeed, mono- and divalent atoms can replace one another as units bound to a central atom without changing the character of the compound (though naturally with a change in valency of the complex). The chlorosulphonates and the permanganates, the difluorophosphates and the perchlorates, and the monofluorophosphates and the sulphates are thus very similar³³.



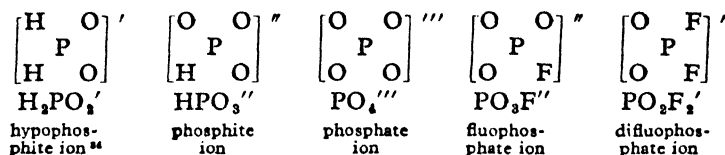
Just as for compounds of the first order, therefore, it is merely schematic to think of the bonding electrons of a semi-polar link as shared equally between the two atoms, the one atom being invested with an excess of one unit of positive and the other atom with an excess of one unit of negative charge. If this is done, the chlorine in the ClO_4' ion, for example, has the charge $(7+) - (4-) = 3+$, and the sulphur in the SO_4'' ion the charge $(6+) - (4-) = 2+$. The numbers so obtained have only a formal and no real meaning.

True double bonds do not occur inside complexes. Here also, as with compounds of the first order, the symbolism involving semi-polar bonds is not at times completely satisfying, that is, where mesomerism may exist, as in the CO_3'' and NO_3' ions (for further, see p. 94).

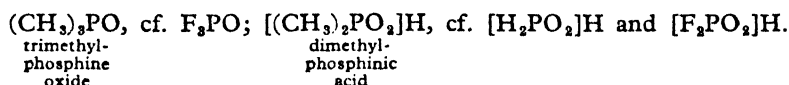
Hydrogen can also be found among the units bound in complexes. In this it is able, unlike all other atoms which can attach themselves to central atoms, to play a *double rôle*. That is, it can approach the electron pair of a central atom as a positively monovalent proton, or it can complete its electron shell to a helium shell with the help of one electron originating from the central atom. In the first case it behaves like an electropositive element as in $\text{H}^+ - \text{Cl}^-$, the formation of the ammonium ion $\text{NH}_3 + \text{H}^+ = \text{NH}_4^+$ and the hydroxonium ion $\text{H}_2\text{O} + \text{H}^+ = \text{H}_3\text{O}^+$ being instances, whereas

³³ W. LANGE, *Ber.*, 1929, 62, 786; 793.

at other times it behaves more like an electronegative element contributing its electron to a homopolar bond, as in the hydrides of the alkali and alkaline-earth metals, for instance, LiH. As such it can take the place of halogens or oxygen, as the following series demonstrates :



The alkyl groups can also play the same dual rôle, showing electropositive character in $\text{CH}_3^+ - \text{Cl}$ and electronegative in $\text{CH}_3^- - \text{Na}$. With them the series can be followed further:



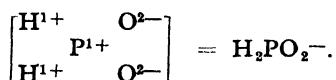
The alkyl groups in the amines instanced by $[(\text{CH}_3)_4\text{N}]\text{Cl}$ are electropositive in nature. To what extent the bonding electrons in the homopolar bonds between the alkyl groups and the central atom are drawn towards or away from the latter must be left open as long as no experiments have been made to measure the polar character of such bonds. The same also holds for the bonds to hydrogen in complexes.

Complexes which contain hydrogen bound homopolarly to the central atom occupy a special place, inasmuch as the compounds derived from them are not always derivable from two independently existing compounds of the first order. It is thus by all means possible to think of hypophosphorous acid as formally originating from $\text{P}_2\text{O} + 3\text{H}_2\text{O}$, just as phosphoric acid originates from $\text{P}_2\text{O}_5 + 3\text{H}_2\text{O}$, but, in contrast to P_2O_5 , the oxide P_2O is not known. In addition, the following difference exists in their derivation. All the hydrogen atoms in phosphoric acid are ionic and thus possess the same electropositive character as in water. But with the reaction written formally as $\text{P}_2\text{O} + 3\text{H}_2\text{O}$, two-thirds of the hydrogen atoms change their character on their transference from the water to the hypophosphorous acid. For the realizable reaction $\text{P}_2\text{O}_3 + 3\text{H}_2\text{O} = 2\text{H}_3\text{PO}_3 = 2\text{H}_2[\text{HPO}_3]$, the proportion is one-third.

For this reason, the usual scheme for reckoning the valency of the central atom, which depends upon referring the compounds of higher order to those of the first order, is denied to compounds of this type with homopolar hydrogen in the complex. In order to conform to the said scheme, phosphorus in hypophosphorous acid according to the process $2\text{H}_3\text{PO}_2 - 3\text{H}_2\text{O} = \text{P}_2\text{O}$ (analogous to $2\text{H}_3\text{PO}_4 - 3\text{H}_2\text{O} = \text{P}_2\text{O}_5$) would have to be monovalent.

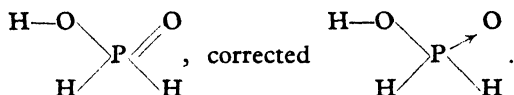
⁸⁴ In the lattice of $\text{NH}_4\text{H}_2\text{PO}_3$, the ion $\text{H}_2\text{PO}_3'$ forms a distorted tetrahedron with the following distances and angles: $\text{H} \begin{array}{c} \text{O} \\ \nearrow \\ \text{P} \\ \searrow \\ \text{H} \end{array} \begin{array}{c} 120^\circ \\ \\ 92^\circ \end{array} \text{O}$, $\text{P}-\text{O} = 1.51$, $\text{P}-\text{H} = 1.5 \text{ \AA}$.
W. H. ZACHARIASEN and R. C. L. MOONEY, *J. Chem. Phys.*, 1934, 2, 34.

The same result is obtained if hypophosphorous acid is thought of as built up of ions, the oxygen being reckoned as negatively divalent and the *hydrogen as positively monovalent*:

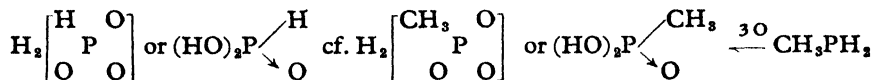


Neither procedure is permissible here, however, since both presuppose that hydrogen be reckoned as an electropositive element, this being immediately obvious in the second procedure, and conditioned in the first by the fact that the hydrogen in the subtracted water is the electropositive partner. Their inadmissibility also follows from the fact that a valence-line formula for hypophosphorous acid with monovalent phosphorus, from which only one valence-line proceeds, cannot be constructed.

If, on the other hand, the analogy to difluophosphoric acid and the phosphoric acids is brought out, one arrives at the conclusion that the phosphorus in hypophosphorous acid is pentavalent exactly as in the phosphoric acids. On this basis, by observing the rules given previously (p. 78), a valence-line formula can be drawn up which reproduces a correct apportioning of the electrons:



With phosphorous acid H_3PO_3 , as already mentioned, a derivation from the known phosphorus trioxide P_2O_3 and a formulation with trivalent phosphorus is possible, corresponding to the method of preparation from $\text{PCl}_3 + 3\text{H}_2\text{O}$. But, in addition, a formula containing pentavalent phosphorus is possible in the sense of the formula given above for hypophosphorous acid. This brings out the analogy to fluophosphoric acid and the alkylphosphoric acids formed on oxidation of the primary phosphines.



The dibasic nature of phosphorous acid is in harmony with this formulation, for which also still more weighty reasons can be brought into the picture. These are obtained from physical investigations of the state of bonding between the phosphorus and the hydrogen.

Thus the formula of phosphorous acid cannot be derived according to pure systematic principles any more than can the valency of the phosphorus. It is no more a solitary case than is hypophosphorous acid. Characteristic of such cases is that the groups gathered round the central atom are not all of the same kind. The valency deduced for the central atom can only be free from doubt when the groups are dissimilar (cf. p. 84) *if for the latter a similar electrochemical character may be assumed*. With this condition, the

central atom obtains a sense of charge which can be added to its valency. But care must be taken to see in the figure for the positive or negative valency so derived only an approximate dimension of the charge on the central atom. If it is not certain whether all the groups possess the same electrochemical character, then in stating the valency the sense of charge is best left out of consideration; for if groups with positive and negative character are simultaneously present on the same central atom, the assigning of a sense of charge to the central atom without any knowledge of the polarity of the individual bonds is impossible. Thus for carbon compounds in which the direction of the polarity of the C—H bonds is uncertain from the start, and furthermore not necessarily the same in all cases, the valency is reckoned according to the last-named method. The simple example of methylene chloride CH_2Cl_2 illustrates to what contradictions one may otherwise be led. Chlorine possesses a definite electronegative character. If the same is qualitatively assumed for hydrogen, that is, the polarity $\text{C}^+ \text{---} \text{H}^-$ for the C—H bond, the carbon comes out positively tetravalent. But if the hydrogen is reckoned as the electropositive partner and the numbers are schematically added together without considering whether and to what degree the polarity of the $\text{C}^- \text{---} \text{H}^+$ bonds differs from that of the $\text{C}^+ \text{---} \text{Cl}^-$ bonds, the valency so calculated for the carbon is zero.

From the first, such a procedure for reckoning the valency according to a polar scheme is not applicable where homopolar bonds between atoms of a similar type occur. This happens not only for organic compounds and compounds such as hydrogen peroxide and hydrazine, but also in inorganic complexes. As an example, dithionic acid $\text{H}_2\text{S}_2\text{O}_6$ might be mentioned, whose constitution as disulphonic acid $\text{HO}_3\text{S—SO}_3\text{H}$ (Fig. 1), which had

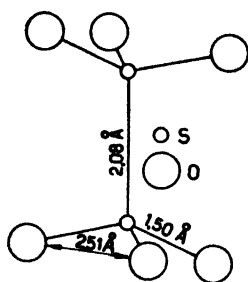


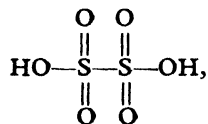
Fig. 1. Structure of the dithionate ion: two inversely situated tetrahedra (Fig. 99, Vol. II) as in the ethane molecule.

long been suspected, is known with certainty from X-ray analysis of its caesium salt ³⁵ and rubidium salt ³⁶. The formal calculation of the valency of the sulphur here leads according to the scheme $\text{H}_2\text{S}_2\text{O}_6 - \text{H}_2\text{O} = \text{S}_2\text{O}_5$ to the non-existent S_2O_5 , from which the valency of +5 follows for the sul-

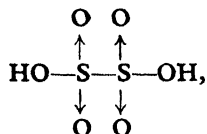
³⁵ G. HÄGG, *Z. physik. Chem.*, 1932, **B 18**, 327.

³⁶ W. H. BARNES and A. V. WENDLING, *Z. Krist.*, 1938, **90**, 153. $\text{K}_4\text{S}_2\text{O}_6$: M. L. HUGGINS, *ibid.*, 1933, **86**, 384.

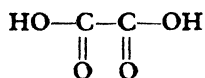
phur. The number +5 does not, however, possess the slightest significance regarding the state of charge of the sulphur in this compound, in which all of its six valence electrons are operative. Corresponding to the formula



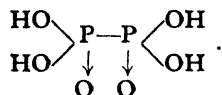
corrected according to the octet rule to



it is to be designated as hexavalent with the same justification that carbon in oxalic acid



is to be denoted as tetravalent. Precisely similar relationships occur in the tetrabasic hypophosphoric acid $\text{H}_4\text{P}_2\text{O}_6$, which is to be written



In it the phosphorus operates all of its five valence electrons ³⁷.

Notwithstanding, for certain practical purposes formal calculations of valency of the kind depicted in the instance of dithionic acid and previously for hypophosphorous acid do possess a meaning. They permit, namely, a direct statement of the number of respective *oxidation* or *reduction equivalents* necessary to arrive at one compound from another, for on such oxidations or reductions the oxygen atoms are put at the disposal of the reducing agent irrespective of how the hydrogen which combines with the oxygen atoms used up was bound previously or how the hydrogen atoms of the reducing agent become bound subsequently. The consumption of oxygen and hydrogen respectively is independent of the type of bonding in which they are involved. Thus, if the valency of the phosphorus in H_3PO_2 is formally reckoned as 1, it is seen that four oxidation equivalents are necessary to oxidize H_3PO_2 to H_3PO_4 . Or if for hydrazine $\text{H}_2\text{N}-\text{NH}_2$, according to

the scheme $\begin{array}{c} \text{H}^+ \quad -_2 \quad -_2 \quad \text{H}^+ \\ \text{N}-\text{N} \\ \text{H}^+ \quad \text{H}^+ \end{array}$, the valency of the two nitrogen atoms is

³⁷ Hypophosphoric acid is formed together with other acids by the slow oxidation of white phosphorus in moist air. Its sodium salt is prepared by the oxidation of red phosphorus by hydrogen peroxide made strongly alkaline with caustic soda.

reckoned as -4 and that of one N as -2 , it is immediately possible to say that oxidation to elementary nitrogen requires four oxidation equivalents and reduction to ammonia with its trivalent nitrogen requires two reduction equivalents. Again, if it is desired to oxidize dithionic acid to sulphuric acid with its positively hexavalent sulphur, then for each sulphur atom which appears to have a valency of $+5$ one oxidation equivalent is needed, that is, two in all. If it is desired to make dithionic acid where the valency of the sulphur is $+5$ from sulphurous acid where the valency is $+4$, then similarly a total of two oxidation equivalents are necessary. The oxidation of dithionate to sulphuric acid is moreover extraordinarily difficult to effect, which speaks against the "pentavalence" of the sulphur contained in it. Dithionic acid, like the analogously built hypophosphoric acid, is stable towards dichromate³⁸, whereas hypophosphoric acid is further not oxidized by nitric acid.

This calculation of the oxidation and reduction equivalents can also be carried out in a way other than that depicted here, in which the number of oxygen and hydrogen atoms required are considered. It is however convenient simply to read off the number of equivalents from the valencies which are assigned to the atoms. Furthermore, the extended concept of oxidation and reduction, which was first developed for changes in ionic charges ($\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$; $\text{MnO}_4' \rightarrow \text{MnO}_4''$; $2\text{Cl}' \rightarrow \text{Cl}_2$; $2\text{SO}_4'' \rightarrow \text{S}_2\text{O}_8''$; $2\text{SO}_3'' \rightarrow \text{S}_2\text{O}_6''$; etc.), thereby simultaneously appears to be universally applicable. Oxidation means a divesting, reduction an assumption of electrons. A change in positive or negative charge corresponds to these processes. The change of charge number is indicated here by a change of valency, which is always stated as a positive or negative number respectively. This reckoning must always agree if hydrogen is consistently included as positively monovalent, since with oxidizing agents it eventually emerges as water or a halogen hydride, in which compounds it is the positive partner.

The definition of valency, which rests on a purely stoichiometric basis, is not always connected in an obvious manner with the number of valence electrons of the elements, in particular when the compounds contain homopolar bonds between atoms of the same kind, or in complexes where the hydrogen is not bound as an electropositive partner. There is now the choice either of giving up the connection between the number fixed for the valency and the number of valence electrons, in which one thinks of the compounds as split up into positive and negative ions with hydrogen always regarded as a positive partner; or of maintaining the connection between valency and number of valence electrons, whereupon the valency is equal either to the number of valence electrons operated or is the difference between this number and 8. In the first case the meaning of valency is always one of charge and cannot be brought into consideration for bonds between two similar atoms where there is no polarity. In the second case the sense of charge may just

³⁸ P. NYLÉN and O. STELLING, *Z. anorg. Chem.*, 1933, **212**, 169.

as well be pronounced as absent. This last-named development of the valence concept means a combination of the definitions of valency first derived independently from the composition of heteropolar and homopolar compounds in inorganic and organic chemistry, and is a better appreciation of the historical development.

In order to avoid the contradiction which appears with the definition of the concept of valency if it is desired to do justice to the stoichiometric viewpoint as well as to its application to homopolar compounds, the suggestion has been made of dropping the concept of valency for homopolar compounds completely, and applying it only where the polar character of a bond is known unquestionably to be more or less strongly pronounced, its place to be taken by a new concept, the *Bindigkeit*³⁹ or "bondability". By bondability of an atom is understood the number of electron pairs by means of which it exists in chemical combination with other atoms. This concept is fixed primarily where one or more electron pairs unequivocally effect a particular bond. The number which expresses the bondability can then be read off directly from the formula. For homopolar compounds this number frequently agrees with the valency with which classical organic chemistry reckons. As a constructional basis for structural formulae, however, it is not able to achieve the same as the classical concept of valency, since it changes more frequently. Also the demand that one or more electron pairs unambiguously effect one particular bond is not always fulfilled, as for example with the nitro group. But since these relations concern organic rather than inorganic chemistry, they will not receive further discussion here⁴⁰.

6. ALFRED WERNER'S Difficulties in Discussing the Valence Concept⁴¹

On surveying the difficulties which even today oppose a universally satisfying definition of valence now that the bonding relationships in compounds of higher order are to a great extent clarified by virtue of the electronic theory of valence, there is no cause for wonder that the explanation of the subject by WERNER, who was without the help of this theory, had in many respects to remain quite unsatisfying. This imperfection in WERNER'S theory, which he himself clearly perceived, was one of the reasons for the slow penetration of WERNER'S correct ideas into inorganic chemistry.

WERNER commenced from the classical concept of valence and the valence-line formulae arising out of it, with the help of which attempts were also made at the time to set down inorganic compounds of first and higher order.

³⁹ B. EISTERT, *Tautomerie und Mesomerie*, p. 21 (*Ahrens Sammlung chem. u. chem.-techn. Vorträge*, New Series, No. 40, Enke, Stuttgart, 1938).

⁴⁰ See, in this respect, W. HÜCKEL, *Der Wertigkeitsbegriff*, *J. prakt. Chem.*, 1943, [ii], 161, 241.

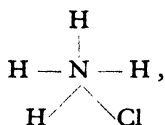
⁴¹ See, in this respect, A. WERNER, *Neuere Anschauungen auf dem Gebiete der anorganischen Chemie* (1st Ed., 1905).

He brought forward weighty objections against these attempts, and was at pains to extend the valence scheme in such a manner that it also became applicable to inorganic compounds of higher order. In three places where manifestly the old valence scheme broke down, he was able to make the necessary adjustment:

- (i) for ammonium salts;
- (ii) for the oxy-, halo- and cyano-acids;
- (iii) for the complex amines and aquo-salts.

From the third point WERNER was led to his centrally constructed co-ordination formulae (nuclear formulae) in place of the chain formulae of BLOMSTRAND (ammoniates) and WURTZ (hydrates), which were formerly in use. This third point is devoid of importance as far as the difficulties in grasping the concept of valency to be discussed here are concerned.

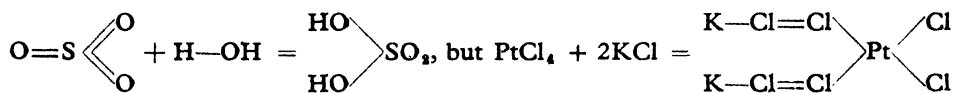
After the formulation of ammonium salts as molecular compounds like $\text{NH}_3 \cdot \text{HCl}$, supported by KEKULÉ among others, had been rejected, they came to be written with pentavalent nitrogen



a formulation which incomprehensibly still survived decades after WERNER'S reform. The "all-equating" joining-line binds the nitrogen to the hydrogen in the same way as to the chlorine, although the latter possesses properties quite different from those in, say, the explosive NCl_3 . That is to say, it is ionic. On the formation of the "compound molecule" $\text{NH}_3 + \text{HCl}$, according to WERNER'S formulation $[\text{NH}_4]\text{Cl}$, a hydrogen atom joins up with the nitrogen atom. But how was WERNER able to explain the bonding of this hydrogen atom to the NH_3 molecule? He knew nothing of the lone electron pair on the nitrogen. Consequently he assumed that besides the three "principal valencies" which bind the three hydrogen atoms in NH_3 , an additional "subsidiary valency" on the nitrogen atom is available which is able to bind the fourth hydrogen atom in the ammonium ion. But since, as WERNER in fact recognized, the NH_4^+ ion is just as symmetrically constructed as the CH_4 molecule, the subsidiary valency from the moment it becomes operative may no longer differ from the three principal valencies. It is the same subsidiary valency which in the metal ammoniates binds the nitrogen to the central atom, although in this case, it is true, an equality of the subsidiary valency and the three principal valencies cannot be spoken of. Even today, such subsidiary-valence bonds are still frequently spoken of, as are also subsidiary-valence rings when two co-ordination positions are occupied by one group. In all these cases, the lone electron pair on the nitrogen assumes a bonding function, in addition to the normal operation of the three valence electrons.

WERNER is also forced to assume an operation of "subsidiary valencies" for the central atom in the halo-acids, as, for example, when the PtCl_4 molecule is converted to the ion PtCl_6^{2-} by the attachment of two chloride ions. Since all the bonds inside the complex PtCl_6^{2-} must be assumed to be equivalent, here again the two subsidiary valencies of the platinum become equivalent to its four principal valencies at the instant of operation. These subsidiary valencies, which manifest themselves with the same strength as the principal valencies and only appear for the appropriate elements on the formation of compounds of higher but never of the first order, indubitably constitute a weakness in the theory which *a priori* differentiates between principal and subsidiary valencies. WERNER was also quite clear that in this inconsistency he made a concession to the classical theory of valence *in order to rescue the significance of the principal-valence number following from the Periodic System*. However, this inconsistency, the cause of which we now clearly recognize on the basis of the electronic theory (see later), enabled WERNER to clear up other absurdities in the classical scheme of valence. These appeared to him to be of considerably greater consequence.

The formulation of ammonium salts with pentavalent nitrogen, from the chemical standpoint contradictory, was only one of these inadequacies in the old ideas of valence. The recognition of the analogy between the oxy-acids and halo-acids and their respective salts was just as important. Thus, before WERNER, potassium platinichloride was formulated as the double salt $2\text{KCl} \cdot \text{PtCl}_4$, but potassium sulphate as the simple salt K_2SO_4 . Whence this differentiation? From the fact that sulphuric acid and its salts could be formulated as arising through addition to a compound written with a double bond, namely SO_3 , whereas this was impossible for chloroplatinic acid and its salts. For the latter, therefore, inasmuch as there was a desire to make assumptions extending the simple manner of writing as double salts, quite a different kind of formula was chosen (BLOMSTRAND):



(The still older chain formulae of the sulphates and chloroplatinates need not be discussed here.)

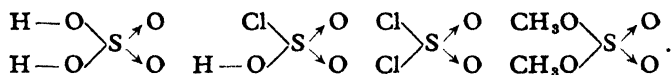
The complex formulae, on the contrary, show up the analogy immediately:



The valence-line convention here works for the oxy-acids with doubly bonded oxygen, which might be expected to possess the same powers of addition in the anhydrides as the doubly bonded oxygen in carbonyls. This suggests itself very readily, but, as we now know, this transference of the symbol of the double bond including its power of addition, which is a property determined for organic compounds, has been one of the serious errors in transferring the valence-line formula from organic to inorganic com-

pounds ⁴². WERNER was not able to *prove* that this was an error, but, on the basis of known chemical facts, *felt it with instinctive certainty* and drew conclusions from it. In this he naturally had no suspicion that in carbonyl compounds the bond is formed through two electron pairs, whereas in the acid anhydrides, as well as in the anions of the oxy-acids, the link between central atom and oxygen is effected by only one electron pair in a semi-polar bond.

The old formulation is by no means completely unjustified if it is confined to the anhydrous oxy-acids, and their salts disregarded. But the formula for the acid must be "corrected" in order to agree with the octet rule, and semi-polar bonds written in place of the double bonds. The acid then comes out analogously to its chlorides and esters:



Corresponding formulae with homopolar bonding of the hydrogen and alkyl groups are not possible for the halo-acids, since with these the surrounding atoms in the complex are only monovalent and thus cannot link themselves by a single electron to any atom other than the central atom. Among these, therefore, no anhydrous acids such as H_2PtCl_6 or HBF_4 are known, only hydrates which contain at least as many water molecules as ionic hydrogen atoms, and which are to be formulated as heteropolar hydroxonium salts, *e.g.*, $[\text{H}_3\text{O}]_2\text{PtCl}_6$. On attempting to withdraw more water from them, they decompose with the evolution of hydrogen halide. Among the oxy-acids there are, in point of fact, similar hydrates which are often very stable, such as $[\text{H}_3\text{O}]\text{ClO}_4$, but water can be withdrawn from them by careful treatment without formation of the anhydride of the acid.

In view of the success which his theory, outlined only briefly here, had over the older notions of valence, WERNER believed he could ignore the weakness in his conception of valence. This lies, as can now be perceived, in the following reasons.

WERNER, like almost every chemist of that period, commenced his considerations from the concept of *affinity between the atoms* as the cause of their combining power. A measure of affinity expressible by a number, the valency, seemed to have been found in the number of monovalent atoms with which an atom was able to unite on the formation of an electroneutral compound (p. 33). If a molecule of this sort still possessed a capacity for the formation of compounds of higher order, then this was supposed to rest on the fact that not all of the affinity had yet been "saturated". Or,

⁴² How deeply rooted this idea was, follows from the fact that in an edition of the text-book by REMSEN and REIHLEN appearing subsequently to 1930, the reaction $\text{Ca}=\text{O} + \text{O}=\text{C}=\text{O} = \text{Ca} \begin{array}{c} \text{O} \\ \diagdown \quad \diagup \\ \text{O} \end{array} \text{C}=\text{O}$ is specified as an example for schools to illustrate the double bond and the application of the valence-line convention. Such formulae also occur on p. 221 among others in the 14th Ed. (1943).

in other words, because the cause of the affinity was regarded to be the "valency", there were still free valencies. These free valencies were expressible, according to WERNER, as subsidiary valencies. In order that these might give rise to a bond, both of the atoms linking up with one another must possess affinity, just as for the bonds involving principal valencies, and each must contribute one valency (multiple bonds can be neglected here) for the formation of the bond. Thus, for the PtCl_6^{2-} ion six valencies from the platinum are to be assumed, four principal and two subsidiary valencies, and in addition six valencies from the chlorine. In $[\text{Co}(\text{NH}_3)_6]^{3+}$ the cobalt exhibits six subsidiary valencies and each NH_3 molecule one subsidiary valency. In $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ the cobalt operates one principal and five subsidiary valencies, each NH_3 molecule one subsidiary and the chlorine one principal valency.

Although WERNER gives no concrete form to his concept of affinity or to the concept of valency regarded as a measure of it, his assumption that for the formation of a bond each of the atoms involved must exhibit affinity, that is, operate a principal or subsidiary valency, is based on the same idea as the primitive classical theory of valence. According to the latter, the formation of a bond can be symbolically illustrated by the linking up of hooks which are thought of as anchored firmly to each atom.

This conception, as we now know, works only for single homopolar bonds where the interplay of electrons originating from neighbouring atoms effect the bond. Alternatively the bonding electron pair can originate from one atom alone. Hence the assumption of six mysterious "subsidiary valencies" for cobalt on the formation of the ion $[\text{Co}(\text{NH}_3)_6]^{3+}$, reducing themselves to five for $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ and four for $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$, is not necessary; nor is the assumption of two subsidiary valencies for platinum in the PtCl_6^{2-} ion, since both of the chloride ions adding on to the PtCl_4 bring with them the electron pair necessary for the bond. WERNER's inconsistency with respect to the dominating theory of valence, which he created by introducing subsidiary valencies, was not a serious error. It can easily be accounted for by the imperfection of contemporaneous knowledge concerning chemical bonds. Without requiring to touch upon WERNER's fundamental thoughts concerning the structure of compounds of higher order, there proved to be no difficulty in removing this inconsistency as knowledge advanced.

7. Structural Thinking in Inorganic Chemistry

Structural-chemical considerations in inorganic chemistry as compared with organic chemistry are relegated very much to the background. There are several reasons for this. The principle of atomic linking upon which structural chemistry is founded has also a wide field of applicability to inorganic chemistry, even if not so exclusively as to organic chemistry, that is to say, in every case where neither decidedly heteropolar compounds nor alloys

are being dealt with. But even here it has not acquired the same meaning for research that it has in organic chemistry. The reason for this is to be sought in the fact that the manner of atomic linking is here hardly ever disclosed with certainty purely by chemical experiment as it is in organic chemistry, but is only ascertained with the aid of a decidedly physical experimental technique. If one wishes to understand the significance of the structural manner of thinking to inorganic chemistry, it is necessary to know just where its application makes sense, and further, whether it is able to give a stimulus to experimental investigation in such cases, and if so, what.

The fields to which it can be applied have already been outlined. There remain essentially all the more or less volatile inorganic substances. Among heteropolar compounds, it also makes sense to speak of a structure for ions built up of a larger number of atoms, in the sense of the organic structural theory. Instances for this are the dithionate and hypophosphate ions which, with their S—S and P—P bonds respectively, are to be written analogously to the oxalate ion containing the C—C bond (p. 82 ff).

But as soon as it is desired to proceed to ascertain such a structure by chemical methods, as in organic chemistry, it is seen that one assumption which can usually be made almost unhesitatingly in organic chemistry is almost never fulfilled. And this is the very assumption which makes a reliable determination of the structure at all possible, namely the *principle of least possible change in structure with chemical reaction*. Its validity for organic compounds is proved by the fact that the structures determined by various ways are the same. The necessity of such a control follows from the observation that sometimes the same structures are not provided, and that therefore the principle can break down. For inorganic compounds there is a choice of ways for gaining the knowledge concerning the manner in which atoms are linked together. This choice is, for the most part, unusually limited, there being usually only one method available. Here, therefore, a control whether or not the principle of least possible change in structure is in force is in general not at all possible. In many cases, moreover, on account of the small number of atoms for which the arrangement of linking is to be ascertained, it is from the first highly improbable that the principle can be applied, for with a structure existing of only a few atoms, chemical attack at any point will not be without influence on the neighbouring atoms. Thus a *rearrangement* has to be reckoned with much more frequently than in organic chemistry. Further, the very phenomena which in certain cases in organic chemistry render the determination of the constitution by chemical methods more difficult, and sometimes even impossible, frequently exclude this totally for inorganic compounds. These phenomena include *tautomerism* through the wandering of a hydrogen atom with bond displacement, and *mesomerism*, that is, the occurrence of a state of combination only imperfectly expressible in a structural form by two or more limiting structural formulae.

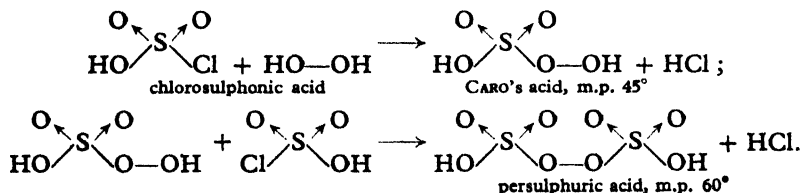
An uncertainty is really always inherent in the structural formulae of inorganic compounds obtained without the help of physical investigations. This can only be removed by the application of non-chemical methods of research. The formulae can supply valuable guidance concerning the use of these methods, and will be duly proved or rejected. By chemical means, if through the use of the principle of least possible structural change they are at all successful, one usually obtains reaction formulae for a compound illustrating a mode of formation or a double decomposition, or sometimes several. Frequently, such reaction formulae have proved themselves to be unshakable in the face of a thorough physicochemical investigation, often, however, not.

As examples of structural formulae derived by chemical methods which have subsequently been proved correct, the structures of the anions of some of the acids of sulphur might be mentioned, namely those of persulphuric acid S_2O_8'' , dithionic acid S_2O_6'' and tetrathionic acid S_4O_6'' . All of these ions can arise in the same way, namely by the partial removal of charge from the corresponding monomeric ions SO_4'' , SO_3'' and S_2O_3'' at the anode during electrolysis. It is admittedly uncertain here whether, in the formation of persulphate and dithionate, the acids are not the primary reaction products, these being able to result by the association of discharged acid ions: $2HSO_4' \rightarrow 2HSO_4 \rightarrow H_2S_2O_8$; $2HSO_3' \rightarrow 2HSO_3 \rightarrow H_2S_2O_6$. But this is of no consequence in the discussion that follows.

The union of two SO_4' to S_2O_8'' (or likewise of $2HSO_4$ to $H_2S_2O_8$), if rearrangement is eliminated, can only succeed through the linking up of the two radicals with one another through a pair of oxygen atoms, since in both the sulphur atoms are completely encased by four oxygen atoms:

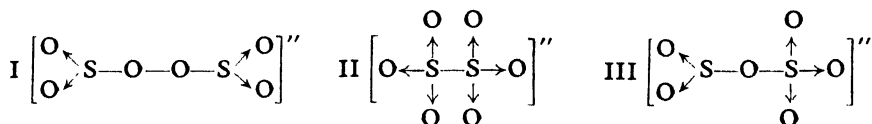


The persulphate ion must therefore be a derivative of hydrogen peroxide if its formula is written $H-O-O-H$. Other modes of formulation and reactions of persulphates are in agreement with this, as is its relationship to CARO's acid H_2SO_5 , which is likewise a derivative of hydrogen peroxide. Of these, only the following synthesis of persulphuric acid, the course of which is clear, will be mentioned:

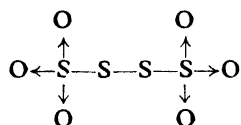


For the dimerization of SO_3' to S_2O_6'' (or likewise of HSO_3 to $H_2S_2O_6$), as also of S_2O_3' to S_4O_6'' , a joining up by means of two sulphur atoms as well as by two hydrogen atoms is conceivable, or even in the last resort

by one oxygen atom and one sulphur atom. Thus the following formulae are possible for the dithionate ion:

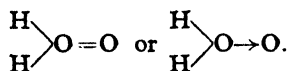


Of these formulae, the last (III) has never been discussed, since no reasons can be put forward in support of the asymmetry. The first has been discarded because dithionates, in contrast to persulphates, are not related to hydrogen peroxide. Hence formula II has been given preference over all others. For the same reason, a symmetrical formula with linking through sulphur atoms has been chosen for the tetrathionate ion, that is to say, a persulphide and not a peroxide structure:



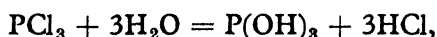
But the formulae are by no means proved by the foregoing arguments. That is only possible by physical methods.

Even the formula HO—OH for hydrogen peroxide, upon which that for the persulphates is based, cannot be proved on a purely chemical basis. To be sure, since the time organic derivatives of hydrogen peroxide have been known, which indubitably possess the structures R—O—O—H and R—O—O—R, this symmetrical formula has been given preference over the unsymmetrical



But since the tautomerism $\text{H}-\text{O}-\text{O}-\text{H} \rightleftharpoons \begin{array}{c} \text{H} \\ \diagdown \\ \text{H} \text{O} = \text{O} \\ \diagup \\ \text{H} \end{array}$ is possible, this did not appear by any means to settle the fact that hydrogen peroxide could be assigned the symmetrical formula. Here again a final decision could only be achieved by physical means (p. 376 ff).

Another example where a chemical determination of the structure fails on account of the possibility of tautomerism is phosphorous acid. According to its manner of formation by the hydrolysis of phosphorus trihalides,



the structural formula $\text{P} \begin{array}{l} \diagup \text{OH} \\ \diagdown \text{OH} \\ \diagdown \text{OH} \end{array}$ must be assigned to it. On the other hand,

its dibasic nature speaks for the formula $\text{H}_2 \left[\text{H}-\text{P} \begin{array}{l} \text{O} \\ \diagdown \text{O} \end{array} \right]$. The examples of tautomeric possibilities for inorganic compounds containing hydrogen

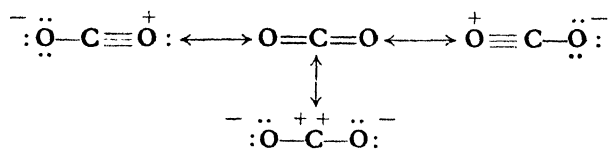
that render impossible the determination of structure by chemical means can be increased at will.

Equally numerous are the cases in which, on account of special bonding relationships and of mesomerism, a satisfactory reproduction of the state of bonding by means of formulae is not possible. Consequently no constitutional formulae are to be drawn up on the basis of chemical reactions. The formulae written $O=O$ and $N\equiv N$, by way of example, which are supposed to indicate the valency of the elements in the molecular state by analogy to the molecular formulae $H-H$ and $Cl-Cl$, where they are justified, do not depict satisfactorily the true state of bonding of the atoms appearing to be bonded to one another by multiple bonds. The $O\equiv O$ "double bond" is indeed, as is now known, effected by four valence electrons, and thus far is not falsely represented by the double line. But as far as the activity of the electrons is concerned, and consequently in its chemical behaviour, it is *not* comparable with the $C=C$ double bond in, say, ethylene, nor with the $C=O$ double bond in aldehydes and ketones. Still less satisfactory is the manner of writing the triple bond in the nitrogen molecule, since this exhibits none of the powers of addition and reactivity of the $C\equiv C$ triple bond in acetylene or of the $C\equiv N$ bond in the nitriles. For the not excessively reactive carbon monoxide, in addition, the formulation $C\equiv O$, or, more completely, $C\equiv O$, cannot provide a correct expression, whether or not it represents an advance over the older formulation with divalent carbon, $C=O$ (p. 422). By it, the analogy in the bonding of the carbon monoxide and nitrogen molecules is stressed when the latter is also written $N\equiv N$ or $:N\equiv N:$, but the inability of the valence-line formula to make statements concerning the kind of electronic activity exists as much in the one case as in the other. What has here been explained for O_2 , N_2 and CO holds also for other molecules constructed of only a few atoms, such as NO , NO_2 , N_2O , etc. (for further, see Chapter VI, pp. 423, 425 ff).

These cases lead to structures in which, in consequence of *mesomerism*⁴³, the exact representation of the condition of bonding by a structural formula is not possible. With inorganic compounds, a mesomerism of this kind has therefore frequently to be reckoned with on account of the small number of atoms in the molecule or ion, in which the bonds very strongly influence one another. A particularly simple case, that of carbon dioxide and the carbonate ion, might suffice as example. Carbon dioxide can be written with two double bonds, $O=C=O$, this also permitting a correct representation of certain reactions the molecule is able to undergo, for example, its reaction with GRIGNARD compounds. The $C\equiv O$ double bond, according to this, would be analogous to that of the carbonyl group $>C=O$ in aldehydes and ketones. However, carbon dioxide is so inert towards almost

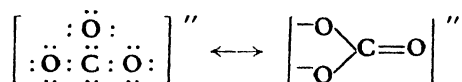
⁴³ For a thorough definition of the concept of mesomerism, see Chapter VI.

all the characteristic carbonyl reagents, that it will not react with them at all. Consequently the existence of the usual C=O bond may reasonably be doubted. The justification for this doubt is provided by the determination of the distance between the carbon and oxygen, which in carbon dioxide amounts to only 1.15 Å⁴⁴ as against 1.22 Å in carbonyl compounds⁴⁵. In reality the electron distribution operative in the carbon dioxide molecule lies between the formulae *:



(for more details, see p. 427).

Likewise the following formulae for the carbonate ion CO₃²⁻ possess a meaning only as limiting cases:



and similarly for the two other oxygen atoms (for more details, see p. 429).

As already stated, working with structural formulae in inorganic chemistry does not possess the same meaning as in organic chemistry, because more frequently the state of bonding cannot be satisfactorily represented by valence-line or electronic formulae. And even where an unambiguous structural formula can be ascertained with the aid of physical methods, often enough it will not allow all the reactions to be illustrated by "reaction formulae", and conversely cannot be derived unequivocally from a study of the reactions. The substitution of formulae based on the electronic theory of valence for the old valence-line formulae does nothing to alter this state of affairs. It represents an advance only in so far as certain erroneous conceptions regarding the kinds of linkages between particular atoms, which arise from the valence-line formulae, are not allowed to appear in the electronic formulae; and that almost entirely by virtue of the application of the octet rule to the latter.

The establishing of an inorganic structural formula, however it is written, is scarcely ever as simple or as convincing as in organic chemistry, and demands a much closer consideration of the most varied chemical and physical observations, as well as a careful weighing up of all the arguments for or against any one of the alternative structures constructed on paper. The beginner, who cannot possibly have the correct feeling for the conclusiveness

⁴⁴ C. FINBAK and O. HASSEL, *Arch. Math. Naturvidenskab*, 1941, 45, No. 3 = *Chem. Centr.*, 1942 I, p. 2236 (electron diffraction).

⁴⁵ D. P. STEVENSON, H. D. BURNHAM and V. SCHOMAKER, *J. Am. Chem. Soc.*, 1939, 61, 2922 (acetaldehyde); D. P. STEVENSON, J. E. LUVALLE and V. SCHOMAKER, *ibid.*, p. 2508 (formaldehyde).

* But see translator's note, p. 434 ff.

of this or that argument, must therefore approach inorganic structural formulae with an uncertainty that even the experienced investigator still possesses with respect to a whole series of formulae for which experiments have so far yielded no adequate criteria. If, in consequence of mechanical study or dogmatical tuition, no such sense of uncertainty develops, then a danger exists of overrating the formulae learnt, as well as of wrong application and highly imaginative speculation in the construction of new formulae. The history of inorganic chemistry up to the most recent times provides examples illustrating that this danger also applies to more mature investigators, and not only to beginners.

Structural-chemical thinking in inorganic chemistry must therefore be harnessed quite otherwise than in organic chemistry. In this there exists a division between the two fields of chemistry, which, in the eyes of many, cannot to all appearances be bridged. Yet, with a superior perspective in structural-chemical thought, it is possible to include both fields in a unified theory of structure, which from the outset thinks in terms of space, namely *stereochemistry*. This has in the broadest sense to comprise the arrangement of the atoms in space and the bonding relationships predominating between them. The classical organic stereochemistry, in which a single atomic model, the tetrahedron, and the valence-line practically suffice, is only a small section of the whole, as is likewise the classical stereochemical idea of WERNER concerning the spatial structure of complexes. The chemical concept of *structure*, extended by the inclusion of bonding relationships to the concept of *constitution*, must be combined with the crystallographical concept of lattice structure in order to be made fruitful when applying it to inorganic chemistry, in which there are relatively few volatile substances. The requirements of structural-chemical thinking in inorganic chemistry include the greater part of that field which has recently come to be known by the name *crystal chemistry*. Since the development of the theory of crystal structure was, in the main, accomplished by crystallographists, mineralogists and physicists, the lattice theory comes more to the fore in the usual presentation, while the chemical problems are largely relegated to the background. For his purpose, the chemist requires a different arrangement of the material, indeed, desires from the outset another point of contact which links on to the observations first made by him, and establishes connections bridging the gap to his own fields of activity. The latter are likewise within the sphere of inorganic chemistry, but far removed from crystal-chemical research. In the same way that the organic chemist finds little satisfaction in a presentation of his field proceeding from an over-emphasized physicochemical basis, the inorganic chemist is not impressed by a crystal chemistry which begins with the spatial lattice theory and subordinates everything to this. Naturally, if he wishes to occupy himself with problems touching upon crystal chemistry, he will have to employ the lattice theory, and can also make much use of a presentation of the said kind. But

in the first place he will ask himself how, starting with chemistry, one arrives at crystal chemistry, just as the organic chemist must ask himself how one arrives at physical chemistry from organic chemistry. Since the chemist starts with matter and not with geometrical form, the necessity of concerning himself with the latter becomes apparent only when he sees that he can no longer do justice to the facts with the theoretical and experimental aids he has so far employed. In this manner, organic stereochemistry originated in its time through a logical development of the KEKULÉ-COUPER structural chemistry. In precisely the same way, one is led to crystal chemistry by a planned extension of WERNER'S co-ordination theory along a path first indicated by P. PFEIFFER. In building thuswise, all sorts of bricks are included which would be left on one side by those commencing with crystallography. This is especially true of the problem of the chemical bond, for which a thorough knowledge of the structure of the atom cannot be dispensed with. If a simile be permitted, one could say that in the construction of the mansion of crystal chemistry, the crystallographers are the architects and contractors, the physicists the brick-layers and the chemists the constructional engineers. The collaboration of them all is necessary if the building is to stand. An instance in science showing how necessary such collaboration is, is the example provided by the geometrical stereochemistry of K. WEISSENBERG in 1925⁴⁶. WEISSENBERG attempted to explain organic stereochemistry on a purely geometrical basis without bothering about the experimental results of the organic chemist. The building supported by only a single experimental determination crumbled in pieces when this was shown to be in error⁴⁷.

It is now especially important that it be demonstrated on the part of the chemist what is of special significance for him in crystal chemistry, and to what knowledge obtained by him through other methods it can be successfully linked; this in order that a building finally results which can serve as a universal theory of structure or as a general stereochemistry embracing crystal chemistry on the one hand and the classical organic as well as inorganic stereochemistry on the other. To bring the chemist inside he would have to be allowed to enter by the door nearest to his dwelling. This door is the systematization of inorganic compounds and the co-ordination theory, the principles of which have already been sketched. Here this theory becomes more closely linked with the results of X-ray analysis of crystalline substances than was possible in its former presentation of less recent date. The systematic viewpoints behind the stereochemical results and also behind those concerning the state of bonding must thereby recede into the background.

⁴⁶ See, for example, *Naturwissenschaften*, 1927, **15**, 662; *Ber.*, 1926, **59**, 1526.

⁴⁷ H. SEIFERT, *Sitzungsber. preuss. Akad. Wiss.*, 1927, **34**, 289; A. SCHLEEDE, G. JUNG and A. HETTICH, *Z. physik. Chem.*, 1929, **B 3**, 479; I. NITTA, *Bull. Chem. Soc. Japan*, 1926, **1**, 62; S. B. HENDRICKS, *Z. Krist.*, 1927, **66**, 131. Reviews: K. LONSDALE, *Phil. Mag.*, 1928, [vii], **6**, 433; S. F. MARRIAN, *Chem. Rev.*, 1948, **43**, 149.

CHAPTER III

THE CO-ORDINATION THEORY OF COMPLEX COMPOUNDS

PART I. MONONUCLEAR COMPLEX COMPOUNDS

1. The most important Types of Compounds: Complex Salts and Double Salts

For the application of WERNER's systematization to complex compounds, a knowledge of atomic complexes is necessary, these having to be arranged in the system according to their structure. By far the greater proportion of complexes are complex ions. In so far as they occur in soluble salts or in insoluble saltlike compounds bearing unequivocal genetic relationships to soluble salts, their formation is recognized, as is generally known, by the following criteria:

A solution of the salt does not give (or, alternatively, only to a slight extent, or only very slowly) the reactions of the individual ions or the reactions of the component parts building up the complex.

Examples: $K_4Fe(CN)_6$ gives only the reactions of K^+ , but not those of Fe^{2+} or CN^- ; $[Co(NH_3)_6]Cl_3$ gives only the reactions of Cl^- , but not those of Co^{3+} or NH_3 .

In double-decomposition reactions involving complex salts, the complex is preserved.

Example: $[Co(NH_3)_6]Cl_3 + 3AgNO_3 = [Co(NH_3)_6](NO_3)_3 + 3AgCl$.

The molecular freezing-point depression indicates the number of ions into which the complex salt splits up. Thus for $K_4Fe(CN)_6$ it is five times as large as would correspond to one molecule of $K_4Fe(CN)_6$ and not eleven times as would correspond to a breaking up into $4K^+$ plus $1Fe^{2+}$ plus $6CN^-$.

The molecular conductivity leads to the same number of ions as the depression of freezing point.

By reason of these characteristics, it is possible to differentiate complex salts from double salts which, in aqueous solution, break down practically completely into their individual ions, whose reactions they give; for example, $KCl.MgCl_2.6H_2O$ dissociates into K^+ , $Mg(OH_2)_6^{2+}$ and $3Cl^-$.

To what extent the fact must be admitted that, under certain circumstances, complexes likewise to a small extent exhibit the reactions of their components,

is shown by the existence of transitions between complex salts and double salts in the salts containing less stable complexes. The characteristic degree of ionic dissociation for the breaking up of a complex can be determined with the help of a series of concentrations.

All these marks of identification are with respect to aqueous solutions. Where an apparent complex compound cannot be brought into solution, the marks by which the existence of a definite complex is identified are much less obvious. In general, one is then dependent on an investigation of the structure in the solid state.

The application of WERNER's co-ordination theory to the crystalline state, which was first undertaken by P. PFEIFFER and later extended by P. NIGGLI (p. 61), meant the biggest advance in WERNER's systematization since their enunciation. In the crystalline state, not only do the complexes known in aqueous solution recur, but, quite generally, also the co-ordination schemes of the WERNER theory in the types of crystalline structures met with. Thus, in the lattice of rock salt, the sodium ion is octahedrally surrounded by six chloride ions and conversely, so that a combination of the complexes $[\text{NaCl}_6]$ and $[\text{ClNa}_6]$ can be spoken of. A further extension of considerations of this sort has been undertaken principally by NIGGLI, who has also introduced symbols distinguishing the co-ordination numbers in the lattice. The nomenclature for the rock-salt lattice may here serve as sufficient example. This is symbolized in an easily understandable manner with a cubically octahedral $[\text{NaCl}_{6/6}]$ lattice structure. The co-ordination numbers for sodium and chlorine will be found here under the Cl symbol in the index.

The octahedron recognized in the lattice is termed the *co-ordination polyhedron*. Different polyhedra, from which the lattices can be constructed, occur in different lattices; for example, tetrahedra and cubic octahedra. If the co-ordination polyhedra are not symmetrical, but can be derived from regular polyhedra by deformation, this is given expression by use of the prefix *pseudo-*.

The co-ordination relationships extant in the lattice of sodium chloride are abolished on dissolving the salt in water. Hence, speaking quite generally, it is highly probable that more co-ordinate bonds occur in the lattice than appear with the ions in solution. Because of this, many double salts may well be complexly bound in the lattice. Changes in colour which are observed on their formation seem to support this. Thus lithium cupric chloride $\text{LiCl} \cdot \text{CuCl}_2 \cdot 3\text{H}_2\text{O}$ is red, and likewise potassium cupric chloride $\text{KCl} \cdot \text{CuCl}_2$, although anhydrous cupric chloride is a yellowish brown. According to this, the salts would probably be more correctly written $[\text{Li}(\text{OH}_2)_3][\text{CuCl}_3]$ and $\text{K}[\text{CuCl}_3]$ respectively. But in aqueous solution they dissociate into the ions Li' or K' respectively, Cu'' — more correctly $\text{Cu}(\text{OH}_2)_4''$ — and $3\text{Cl}'$, whereupon the complex $[\text{CuCl}_3]'$ is hydrolyzed by water. With KCuCl_3 this hydrolysis sets in even in moist air, and for the same reason the corresponding sodium salt cannot be prepared at all, while the garnet-red caesium

salt CsCuCl_3 ¹, on the contrary, is stable in moist air. The blue "double salt" $2\text{KCl}\cdot\text{CuCl}_2\cdot 2\text{H}_2\text{O}$, which can be written as a loose complex, that is, as the tetrachloro-diaquo-salt $\text{K}_2\left[\text{Cu}\begin{matrix} (\text{OH}_2)_2 \\ \text{Cl}_4 \end{matrix}\right]$ (but cf. p. 137 ff) — the corresponding fluoride is also known — is formed in addition to $\text{CuCl}_2\cdot 2\text{H}_2\text{O}$ (see p. 137) on hydrolysis of KCuCl_3 . With carnallite, however, nothing of this sort occurs, since the $6\text{H}_2\text{O}$ in the crystal lattice indicates that the magnesium contained in it forms its characteristic hexaquo-cation, as in bischofite $[\text{Mg}(\text{OH}_2)_6]\text{Cl}_2$.

For insoluble double salts, a further special definition is necessary in order to be able to identify them in the lattice as individual compounds, as the example of dolomite $\text{MgCO}_3\cdot\text{CaCO}_3$ will illustrate.

Dolomite crystallizes rhombohedrally like calcite, but does not possess its perfect cleavability. The cleaved rhombohedron obtained from it has the angle 107° , thus differing sufficiently from the calcite rhombohedron with angle 105° for no extensive miscibility to exist between dolomite and calcite. There is likewise a miscibility gap in the direction of magnesite. In the stoichiometrically combined dolomite, the calcium and magnesium ions are distributed regularly in the lattice positions between the carbonate ions. Since a replacement of Mg^{++} by Ca^{++} and *vice versa* can occur to a slight extent only, dolomite is a substance with its own crystal structure and is to be designated in the crystalline state as a double salt. From the point of view of the phase rule, a saltlike compound formed from two single salts is accordingly to be spoken of in the lattice as a double salt and a discrete compound if it is separated from the components by a decided gap in the miscibility.

Complex compounds are best subdivided in the first place according to the number of co-ordination centres. One has thus to distinguish between mono-, di- and polynuclear compounds. The polynuclear compounds lead to those substances whose complex structures can be understood only by a consideration of the whole crystal lattice, like heteropoly- and isopolyacids, or prussian blue. Among the mononuclear compounds and ions, the substances are most simply arranged according to the co-ordination number of the central atom.

A reproduction of the material which has been systematically ordered in this way need not be repeated here². Those aspects which facilitate a deeper insight into the structure of complexes should, however, be stated.

To these belong the inclusion of the crystalline state in the field of application of WERNER's co-ordination theory. This further provides for a com-

¹ For the structure, see A. F. WELLS, *J. Chem. Soc.*, **1947**, p. 1662 (cf. p. 129). Lithium cupric chloride, which contains water of crystallization, apparently possesses a different lattice structure.

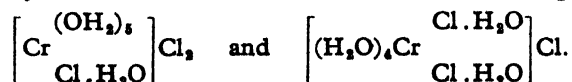
² A comprehensive presentation is given in R. F. WEINLAND's *Einführung in die Chemie der Komplexverbindungen* (2nd Ed., Enke, Stuttgart, 1924). See also the fundamental work of A. WERNER, *Neuere Anschauungen auf dem Gebiete der anorganischen Chemie* (4th Ed., 1920, revised by P. PFEIFFER).

parison of complexes, as derived from their behaviour as salts in aqueous solution, with complexes in the crystal lattice. The universal standpoint would be to begin with the latter. According to this, the breaking up of the lattice during the process of dissolution becomes a part of the problem concerning the reactions of crystalline substances. The numberless water-insoluble complex compounds, such as the silicates, would likewise be included at the outset. With respect to the understanding, however, it does not appear advantageous to begin with considerations which in part make quite considerable demands on the powers of conception. Rather it would be more useful to follow the historical development and fix attention first on the spatial relationships in complex compounds formed from a small number of atoms and complete in themselves, that is to say, in complexes as they arise on the dissolution of many complex salts in water. In this manner, by following the advance in knowledge for which PFEIFFER paved the way, relations between these complexes and the lattice structures can nevertheless be pointed out in various ways. It can also be shown by suitable examples that the WERNER co-ordination number in saltlike complexes, as given by the stoichiometric formula of a complex salt, does not always need to agree with the co-ordination number in the lattice. This combination of the classical inorganic "chemistry of solutions" with crystal chemistry becomes more firmly knitted in passing step by step from the mono- to the polynuclear compounds, and from these to the poly-acids. But a survey of the most important types of complex compounds will be given first.

Certain phenomena concerning isomerism in complex ions lead to conceptions of the spatial structure of complexes. This corresponds exactly to the way in which certain kinds of isomerism in organic chemistry have led to the development of ideas concerning steric arrangement. Consequently the general problem of isomerism in mononuclear complexes will be dealt with next.

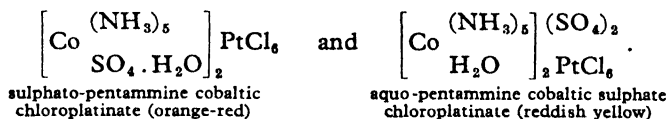
2. Structural Isomerism in Complex Compounds

The structure of the complexes themselves, as well as of the groups which take part in building up the complexes, can lead to isomerism. Isomers occur through different arrangement of the same groups within a complex. The *hydrate isomerism* of the chromium chloride hexahydrates is a well-known example of this kind. There are three different hexahydrates of chromic chloride $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, one violet and two green. The violet salt is hexaquo chromic chloride $[\text{Cr}(\text{OH}_2)_6]\text{Cl}_3$, the two others are hydrates of chloro-pentaquo chromic chloride $[\text{Cr}(\text{OH}_2)_5\text{Cl}]\text{Cl}_2$ and dichloro-tetraquo chromic chloride $[\text{Cr}(\text{OH}_2)_4\text{Cl}_2]\text{Cl}$ respectively, which contain water of hydration loosely bound to the chlorine atoms in the complexes

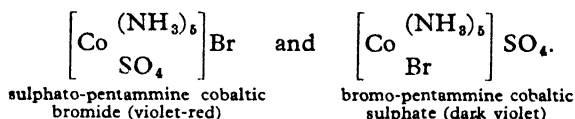


This water can be easily removed in a desiccator. The violet hexahydrate, on warming it in solution with hydrochloric acid, is converted into the green hexahydrates. In the similar instance of the isomeric hydrates of chromous chloride, a molecule of water leaves the aquo-complex and hydrates the anion: $[\text{Cr}(\text{OH}_2)_4]\text{Cl}_2$ (blue) and $\left[\text{Cr} \begin{matrix} (\text{OH}_2)_3 \\ \text{Cl} \end{matrix}\right] \text{Cl} \cdot \text{H}_2\text{O}$ (green). Both salts are formed together by evaporation of the red chromous acetate with concentrated hydrochloric acid under reduced pressure.

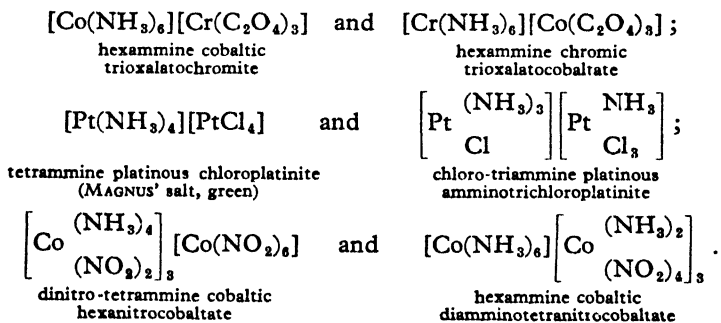
Another example is the isomeric pair:



Another kind of isomerism is *ionic metamerism*, in which the acido groups in the complex and anion appear to be interchanged, for example:



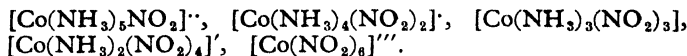
Immediately understandable is the sort of isomerism, named *co-ordination isomerism* by WERNER, which occurs in the instances of the following pairs of compounds:



The last-named salts are incidentally tetramers of trinitro-triammine cobalt



Other kinds of isomers are those which are brought about when the groups inside complexes of the same overall composition possess different structures (Chapter II, p. 62). These isomers correspond completely to the structural isomerism so familiar in organic chemistry. Thus the NO_2 grouping, as in organic compounds, can appear as a nitro group with pentavalent nitrogen linking itself to the central atom by means of the nitrogen, or as a nitrito group with trivalent nitrogen bound to the central atom through an oxygen atom, in the same way as it is bound to carbon in the esters of nitrous acid. Examples of complexes containing nitro groups are the nitro-cobalt compounds of the familiar series:



Isomeric with the yellow nitro-pentammine-cobaltic ion is the pinkish-red nitrito-pentammine-cobaltic ion $[\text{Co}(\text{NH}_3)_5\text{ONO}]^{2+}$. The dinitro- and dinitrito-bis-ethylenediamine-cobaltic salts $[\text{en}_2\text{Co}(\text{NO}_2)_2]^+$ and $[\text{en}_2\text{Co}(\text{ONO})_2]^{3-}$, in which, furthermore, stereoisomerism is known, constitute another example. WERNER named this kind of isomerism *salt isomerism*, a term which in point of fact is scarcely characteristic.

The constitutional proof is here not so easy to execute as in organic chemistry, since chemical reactions which might serve to investigate the structure of complexly bound groups invariably destroy the unity of the complex, as does reduction, for example. Consequently a non-chemical manner of proof is indicated. In the case cited, it is possible to draw conclusions concerning the bonding of the NO_2 grouping to the central atom from the absorption of light. Where bonds involve a nitrogen atom only, as in $[\text{Co}(\text{NH}_3)_6]^{3+}$, the complexes are yellow, and where bonding is through an oxygen atom pinkish red in colour. This pinkish-red colour is always met with in cobaltic complexes if the groups are linked to the central atom through oxygen, as, for instance, in the nitrato-pentammine-cobaltic and sulphato-pentammine-cobaltic salts.

The nitrito-complexes are less stable than the nitro-complexes, as follows from their ready isomerization, which may take place in the solid state as well as in solution. The anion plays an appreciable rôle in the velocity of this process. Thus the nitrate of the $[\text{Co}(\text{NH}_3)_5\text{ONO}]^{2+}$ ion rearranges in the solid state about five times as quickly as the chloride. In solution, increasing restraint is exercised on the isomerization in the sequence HNO_3 , HClO_4 , HCl ^{3a}.

The complexes containing nitro groups are further much stabler towards treatment by mineral acids than those containing nitrito-groups, which latter are thereby replaced by water. This agrees with the behaviour of nitro-compounds and esters of nitrous acid in organic chemistry. Conversely, the nitrito-cobaltic salts are formed easily from aquo-pentammine-cobaltic salts and sodium nitrite in dilute hydrochloric acid ⁴. Nitro-cobaltic salts, on the other hand, are formed from chloro-pentammine-cobaltic salts with nitrite and strong hydrochloric acid, as well as from ammoniacal solutions of cobaltous salts and N_2O_3 . For example, $\text{CoSO}_4 + \text{NO}_2 + 5\text{NH}_3 = [\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{SO}_4$. The familiar potassium hexanitrocobaltate (or cobaltinitrite) $\text{K}_3[\text{Co}(\text{NO}_2)_6]$ is similarly formed from a cobaltous salt and potassium nitrite in acetic acid solution.

An isomerism of the cyano group as it occurs in the nitriles and isonitriles is not found in cyano-complexes. The bonding of the cyano group

³ The symbol 'en' is an abbreviation for ethylenediamine $\text{H}_2\text{N}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}_2$.

^{3a} B. ADELL, *Svensk Kem. Tidskr.*, 1944, **56**, 318; 1945, **57**, 260; *Acta Chem. Scand.*, 1947, **1**, 659; B. ADELL and G. THÖLIN, *ibid.*, p. 624.

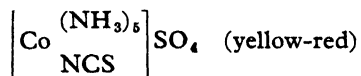
⁴ S. M. JÖRGENSEN, *Z. anorg. Chem.*, 1894, **5**, 168.

to the central atom is effected in all cases so far investigated through the carbon. Proof for this has been substantiated mainly by F. HÖLZL⁵ through alkylation over a fairly extensive field of observation. In this manner, compounds were obtained which invariably gave *isonitriles* on decomposition⁶. The alkyl groups must thus attach themselves to the nitrogen, whereupon it follows that the latter cannot be claimed for bonding by the central atom. Thus, on the alkylation of silver ferrocyanide with methyl iodide or dimethyl sulphate several compounds are formed, all of which give the *isonitrile* or a salt of methylamine on decomposition, but not an ammonium salt. From these, which for the determination of its structure is very important, salts of the hexa-methylcarbylamine-ferrous ion can be prepared, such as the chloride $[\text{Fe}(\text{CNCH}_3)_6]\text{Cl}_2$. On heating to 150° the chloride gives two *isonitrile* molecules bound in the complex: dicyano-tetra-methyl*isonitrile* iron $[(\text{CH}_3\text{NC})_4\text{Fe}(\text{CN})_2]$ and tetra-methyl*isonitrile* ferrous cyanide $[\text{Fe}(\text{CNCH}_3)_4](\text{CN})_2$ — incidentally an interesting case of complex isomerism.

The complexly bound cyano groups in the ferrocyanide are thus completely or partly converted into *isonitrile* molecules on alkylation.

Besides the very thorough investigation of the alkylation of hydrogen ferrocyanide, the alkylation of the octacyano-acids of molybdenum and tungsten has been carried out, as also of the tricyano- and tetracyano-acids of cadmium. Here also the cyano groups are converted into an *isonitrile*.

Isomers containing thiocyanato groupings differently linked, such as occur in the esters of thiocyanic acid $\text{R}-\text{S}-\text{C}\equiv\text{N}$ and the mustard oils $\text{R}-\text{N}=\text{C}=\text{S}$, have not been observed in the complexes, although very numerous thiocyanato-complexes have been prepared. However, the essential point is that the thiocyanato group is contained in many complexes and the *isothiocyanato* group in others. Thus in *isothiocyanato*-pentammine cobaltic sulphate

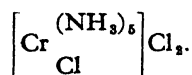


an *isothiocyanato* group is to be assumed, in which the nitrogen atom is linked to the cobalt atom, since on oxidation with chlorine in aqueous solution hexammine cobaltic chloride $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ is formed. Thus, from the *isothiocyanato* group — apparently as a consequence of hydrolysis — ammonia results with the nitrogen likewise bound to the cobalt. On the other hand, the thiocyanato group in the thiocyanato-pentammine-chromic salts is linked to the chromium in a different manner, probably by means of the sulphur,

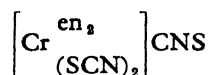
⁵ F. HÖLZL, *Monatsh.*, 1927, **48**, 71; 1929, **51**, 1; 397; F. HÖLZL and G. I. XENAKIS, *ibid.*, 1927, **48**, 689.

⁶ First observed $(\text{C}_2\text{H}_5\text{I} + \text{Ag}_2\text{Fe}(\text{CN})_6)$ by M. FREUND, *Ber.*, 1888, **21**, 931. Later investigations by E. G. J. HARTLEY, *J. Chem. Soc.*, 1910, **97**, 1066; 1725; 1911, **99**, 1551; 1912, **101**, 705; 1913, **103**, 1196. Compilation by F. HÖLZL and S. KIRCHMAYR, *Monatsh.*, 1929, **51**, 397. Two isomeric esters of hydrogen cobalticyanide $\text{H}_3[\text{Co}(\text{CN})_6]$: E. G. J. HARTLEY, *J. Chem. Soc.*, 1914, **105**, 521; F. HÖLZL, T. MEIER-MOHAR and F. VIDITZ, *Monatsh.*, 1929, **52**, 73; **53/54**, 237. Preparation with diazomethane: J. MEYER and O. RAMPOLDT, *Z. anorg. Chem.*, 1937, **232**, 188.

since in this case treatment with chlorine leads to chloro-pentammine chromic chloride



But a strict proof that the bond in this case is effected by the sulphur must not be seen in the unobservable course of the reaction with chlorine. The isomerism of dithiocyanato-bis-ethylenediamine chromic thiocyanate



does not arise through isomerism in the thiocyanato groups, but is a kind of stereoisomerism (see later). The two stereoisomeric dithiocyanato-salts, of which one is reddish orange and the other yellowish orange, give stereoisomeric dichloro-bis-ethylenediamine-chromic salts on treatment with chlorine, of which one series is violet and the other green.

3. Stereoisomerism and Spatial Structure of Mononuclear Complexes and of Compounds of the First Order

Isomers of compounds with the co-ordination numbers 6 and 4 are known whose isomerism can be explained by a different spatial arrangement of the same groups about the central atom. In this explanation, certain assumptions concerning the spatial structure of the complexes are necessary, which may also be transferred to compounds not exhibiting this isomerism as well as to compounds of the first order, although with certain reservations. The existence of a definite number of stereoisomers leads here, as in organic chemistry, to definite spatial models which, in this way, may be well-founded in cases where the co-ordination number is 6 or 4. For the remaining co-ordination numbers, there are as yet no isomeric phenomena known which indicate definite spatial structures. Here other purely physical methods are necessary in order to obtain information concerning the spatial construction of compounds with co-ordination number 2, 3, 5, 7 or 8. Thus, although isomers have not so far been observed in these cases, the stereochemistry of the compounds in which these co-ordination numbers occur should be dealt with in continuation of the ideas of spatial structure of complexes with the co-ordination numbers 6 and 4, as developed on the basis of isomers. Also, for the co-ordination number 4 in particular, purely physical methods have had to be brought in on more than one occasion for solving the spatial structure of a complex.

(i) Spatial Structure of Complexes with the Co-ordination Number 6

The symmetrical arrangement of six groups about a central atom can be effected either as a regular hexagon or at the corners of an octahedron.

Since the number of isomers differs in each case, a decision between the two possibilities can be made on the basis of the number of isomers observed. For the regular hexagon with two groups differing from the rest, three isomers must be possible corresponding to the *ortho*, *meta* and *para* derivatives of benzene. Since these, however, have never been observed, but invariably two only, the facts find a natural explanation in the octahedral representation. The two substituents differing from the others can occur either in the edgewise or in the axial position. In the first case one speaks of a *cis*, and in the latter case of a *trans* configuration (Fig. 2).

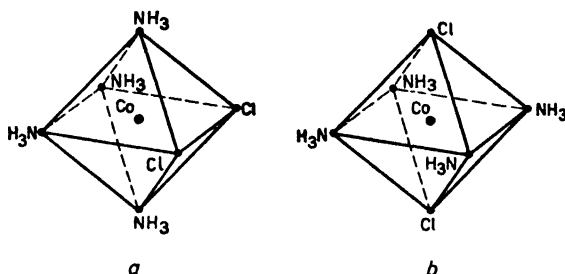


Fig. 2. (a) *Cis* or edgewise position; (b) *trans* or axial position

To the first known examples of this kind belong the isomeric dichloro-tetrammine-cobaltic salts $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$, which are named *praseo*⁷ and *violeo* salts after their colours. The green salts arise from chloro-aquo-tetrammine cobaltic chloride, diaquo-tetrammine cobaltic chloride or carbonato-tetrammine cobaltic chloride on treatment with concentrated hydrochloric or sulphuric acid. Alcoholic hydrochloric acid gives a mixture of the green and violet chlorides. Salts of the violet series also arise from the polynuclear cobaltamines.

Praseo and violeo salts also occur in the dichloro-bis-ethylenediamine series $[\text{CoCl}_2\text{en}_2]^+$.

Corresponding to these there are a yellow-brown *flavo* and a yellow *croceo* series in the dinitro-complexes $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2]^+$ and $[\text{Coen}_2(\text{NO}_2)_2]^+$, as also in the dinitrito-complexes.

The *flavo* salts are formed from carbonato-tetrammine cobaltic sulphate or nitrate and sodium nitrite in nitric acid solution, the *croceo* salts from praseo-dichloro-tetrammine cobaltic chloride and sodium nitrite in acetic acid solution, or similarly from nitro-pentammine cobaltic chloride.

Also for the diaquo-bis-ethylenediamine-cobaltic salts $[\text{Coen}_2(\text{OH}_2)_2]^+$ there are two series, one bright red and the other reddish brown.

Not only with trivalent cobalt, but also with trivalent chromium cases to be explained by *cis-trans* isomerism are known in great number.

⁷ From πράσος (green leek).

Violeo and flavo salts are *cis* compounds, whereas praseo and croceo are *trans*.

Proof of configuration for stereoisomers. — Configurational proof for *cis-trans* isomers can be accomplished by virtue of the fact that the two co-ordination positions, which certain groups such as the carbonato, oxalato and sulphato groups or the diamines can occupy, must invariably occur in the *cis* position. This conclusion corresponds in principle to the behaviour of sterically adjacent groups in organic compounds. If such compounds are now converted into others in which the two co-ordination positions filled by the respective di-substituent are replaced by two single groups, the latter must take up the *cis* configuration. This conclusion is valid only as long as it may be assumed that on the substitution of one group by another, the new group takes up the position of its predecessor. This can by no means be taken for granted, as the occurrence of the WALDEN Inversion in substitutions on asymmetric carbon atoms shows. A special proof whether or not a WALDEN Inversion is to be reckoned with in the reactions applied to the determination of a configuration is consequently invariably required. For complex compounds, the decision is frequently simplified by the fact that *cis-trans* isomers are generally distinguishable on account of a considerable difference in colour, and that the same or similar colour with different groups permits an identical configuration to be inferred. This kind of proof will be illustrated by several examples.

The yellow-brown flavo-dinitro-tetrammine-cobaltic salts are formed from the carbonato-tetrammine salts (see previously); the flavo salts can accordingly be assigned the *cis* configuration provided the nitro groups assume the places of the carbonato group. How careful one needs to be when carrying out such a proof is taught by the example of the praseo and violeo salts which occur together in quantities varying according to the experimental conditions when the carbonato salts are treated. To be sure, WERNER established by special experiments that at very low temperatures the violeo salts are first formed, these on less careful treatment undergoing either complete or partial rearrangement into the praseo salts. From this and also from the cleavage of the dinuclear diol-octammine-cobaltic salts (p. 160), it follows that the violeo salts have the *cis* configuration, again with the same limiting conditions as before. That the latter are not always realized, or rather, that an initial change of position occurs on substitution, is illustrated by numerous instances. One of these is the action of ammonia on *trans*-dichloro-bis-ethylenediamine cobaltic chloride, which provides *cis*-chloro-ammine-bis-ethylenediamine cobaltic chloride. Just as for substitution on an asymmetric carbon atom, the experimental conditions — temperature and concentration — can exert an influence on the extent to which the new group takes the place of the preceding group and the extent to which it does not.

It is therefore of great moment that there should be additional absolute proofs of configuration for certain *cis-trans* isomers, which have also been

utilized to ascertain the configuration just given. These proofs rest upon the resolution of certain configurations into optical counterparts. Thus, for example, the above-mentioned green praseo-*trans*-dichloro-bis-ethylenediamine cobaltic chloride is not resolvable, whereas the isomeric violeo salt is.

Optical Isomerism. — The existence of mirror-image isomers is a further consequence of the octahedral structure of complexes with the co-ordination number 6. Mirror isomerism can arise if the complex contains groups occupying two co-ordination positions. In 1911, WERNER was able to confirm by experiment this prerequisite for optically active complex compounds, and thereby give the strongest support to the octahedral theory.

If the complex contains two groups, each filling two co-ordination positions, mirror isomerism is possible when the two remaining positions have the *cis* configuration. No mirror images are obtained from the corresponding *trans* isomers. In this it is immaterial whether these two co-ordination positions are filled by the same or different groups (Fig. 3). This may be rep-

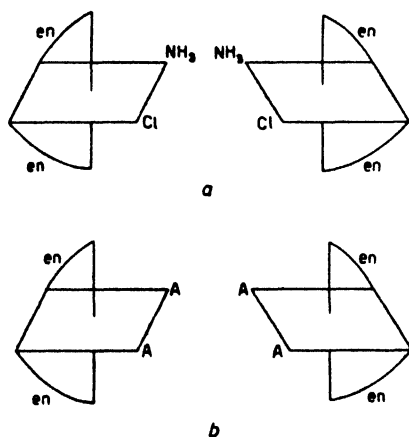


Fig. 3. Mirror isomerism in (a) the *cis*-chloro-ammine-bis-ethylenediamine-cobaltic ion, (b) complexes with two ethylenediamine groups and two other identical substituents.

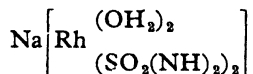
resented by the typical example of the chloro-ammine-bis-ethylenediamine-cobaltic ion, which WERNER resolved by means of the bromocamphorsulphonate⁸. In this way the *cis* configurations of the violeo-dichloro-bis-ethylenediamine-cobaltic ion and the flavo-dinitro-bis-ethylenediamine-cobaltic ion have been demonstrated. There is no absolute direct configurational proof to be executed on the similarly coloured tetrammine compounds. Nevertheless, there is no doubt that they can be designated *cis* compounds with like certainty on account of the characteristic difference in colour of the isomeric forms.

It has yet to be mentioned that the active dinitro-bis-ethylenediamine

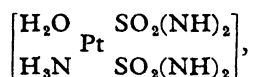
⁸ A. WERNER, *Ber.*, 1911, 44, 1887.

salts do not racemize in aqueous solution, whereas, on the other hand, the dichloro-bis-ethylenediamine salts racemize in a few hours.

To the same type belong the anionic diaquo-bis-sulphamide complex of rhodium⁹



and the aquo-ammine-bis-sulphamide complex of platinum



in which the divalent radical from sulphamide $\text{SO}_2(\text{NH})_2$ occupies two co-ordination positions as the acido group $\text{HN.SO}_2.\text{NH}$. Admittedly only one form is known here. This, at least in the case of rhodium, must be the *cis* form, since with the help of optically active phenylethylamine it has been possible to resolve it into optical counterparts, which are furthermore remarkably stable.

If each of the three groups in a complex occupy two co-ordination positions, the mirror-image isomers appear as follows:

(i) All three groups the same. Examples are the tris-ethylenediamine-cobaltic (likewise trivalent chromium and rhodium) ion $[\text{Co}(\text{en})_3]^{3+}$ ¹⁰ (Fig. 4) and the trioxalato-chromic ion $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$ ¹¹. The active trioxalato-

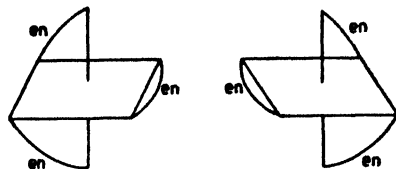


Fig. 4. Mirror-image isomerism in tris-ethylenediamine compounds.

anions racemize rapidly in aqueous solution: their specific rotation is exceptionally high.

(ii) One group differing from the two others. Examples are the carbonato-bis-ethylenediamine-cobaltic salts (Fig. 5) and the oxalato-bis-ethylenediamine-cobaltic salts.

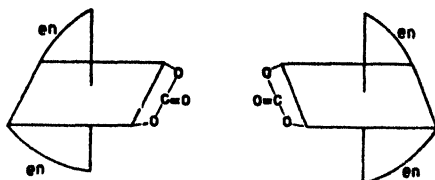


Fig. 5. Mirror-image isomerism in the carbonato-bis-ethylenediamine-cobaltic ion.

⁹ F. G. MANN, *J. Chem. Soc.*, 1933, p. 412.

¹⁰ A. WERNER, *Ber.*, 1912, 45, 121.

¹¹ A. WERNER, *Ber.*, 1912, 45, 3061. The trioxalato-complexes of rhodium, iridium and iron have also been resolved.

This mirror-image isomerism is, at the same time, a proof that the carbonato as well as the oxalato groups occupy two adjacent co-ordination positions.

Mirror-image isomerism is also possible with only one group filling two co-ordination positions, but the four remaining positions must be occupied by two pairs of similar substituents, as is the case in the dinitro-oxalato-diammine-cobaltic ion $[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_2\text{C}_2\text{O}_4]'$ (Fig. 6), for example. Here also it is only the *cis* form which is resolvable. The resolution of this complex

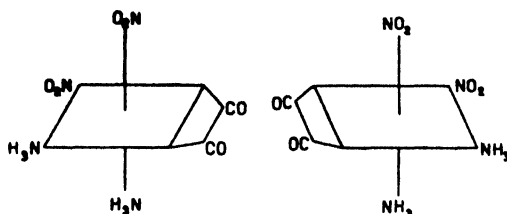


Fig. 6. Mirror-image isomerism in the *cis*-dinitro-oxalato-diammine-cobaltic ion.

into its optical counterparts has been of significance for the determination of the configuration of ERDMANN's salt $\text{NH}_4[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]$, which was in this way proved to be the *cis* compound. This salt cannot occur as optical counterparts, in contrast to the salt formed from it by the replacement of two nitro groups by an oxalato group, which can. To be sure, the proof is not binding, inasmuch as it is based on the supposition that the incoming groups take up the same positions as the outgoing. This condition need not be in force since in other cases (as in the WALDEN Inversion) a change of configuration is observed (p. 106).

The octahedral structure, proved by stereo- and optical isomerism for various instances, was now assumed by WERNER to be quite general for complexes with the co-ordination number 6, including those in which, owing to the similarity of the groups, no proof was forthcoming, in the same way as a tetrahedral structure was assumed for CH_4 and CCl_4 although such a proof is demonstrable only for compounds with four different substituents. This assumption of WERNER's subsequently received a brilliant confirmation when it became possible to ascertain the spatial structure of crystallized complex compounds with the help of X-ray analysis. The first proofs of this kind were carried out by SCHERRER¹² for the instances of K_2PtCl_6 and the analogously constructed $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$, and by WYCKOFF¹³ for $(\text{NH}_4)_2\text{PtCl}_6$ ¹⁴ (see Fig. 68a, Vol. II).

¹² P. SCHERRER and P. STOLL, *Z. anorg. Chem.*, 1922, **121**, 319.

¹³ R. W. G. WYCKOFF and E. POSNJAK, *J. Am. Chem. Soc.*, 1921, **43**, 2292; R. W. G. WYCKOFF, *ibid.*, 1922, **44**, 1239. This structure type occurs elsewhere very frequently, for example, in $(\text{NH}_4)_2\text{SiF}_6$, $(\text{NH}_4)_2\text{SnCl}_6$, $(\text{NH}_4)_2\text{PbCl}_6$, $\text{Mg}(\text{NH}_3)_6\text{Cl}_2$, $\text{Cd}(\text{NH}_3)_6\text{I}_2$. Further examples are given by W. BILTZ, *Raumchemie der festen Stoffe*, p. 48. For a list of a number of salts with the lattice type K_2PtCl_6 , see *Strukturber.* III, p. 121; and for the type $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$, *ibid.*, III, p. 475. For K_2SeBr_6 , as for K_2PtCl_6 , see J. L. HOARD and B. N. DICKINSON, *Z. Krist.*, 1933, **84**, 436.

¹⁴ For further examples of the structures of complex compounds, see G. WITTIG, *Stereochemie*, p. 303 (Leipzig, 1930).

The diffraction of X-rays and electrons has also proved the octahedral structure for compounds of the first order and co-ordination number 6, as for SF_6 ¹⁵, WCl_6 ¹⁶, telluric acid $\text{Te}(\text{OH})_6$ ¹⁷ — hence not $\text{H}_2\text{TeO}_4 \cdot 2\text{H}_2\text{O}$ or $[\text{H}_3\text{O}]_2\text{TeO}_4$ — and the carbonyls of the $\text{Cr}(\text{CO})_6$ class¹⁸. UF_6 , WF_6 and apparently also MoF_6 , on the other hand, have not got a regular octahedral structure, but are rhombic double-pyramids¹⁹.

(ii) Co-ordination Number 4

For the co-ordination number 4, the possible arrangements of the groups about the central atom are tetrahedral, pyramidal and planar. By analogy with the compounds of carbon, a tetrahedral arrangement of the groups is to be expected. As the existence of optically active ammonium compounds and optically active silicon and tin compounds shows, such a state of affairs is also to be assumed for the ammonium ion NH_4^+ , which is constructed exactly like methane CH_4 , and for the silicon compounds such as SiH_4 , SiCl_4 and $\text{Si}(\text{OCH}_3)_4$ ^{19a}, as well as for the analogous compounds of tin. A tetrahedral structure is not quite universal, however, for with certain central atoms, compounds of the type XA_2B_2 are known in two isomeric forms, this being possible only with a *planar* configuration. Complexes with the co-ordination number 4 thus require special investigation in order to ascertain whether their structure is tetrahedral or planar. Chemical methods based on the number of isomers often provide no further assistance here, and one is obliged to draw on physical methods which permit an establishment of the symmetry.

The first isomerism phenomena which WERNER explained by a planar configuration of the complexes were observed with compounds of divalent platinum and palladium^{19b}.

Thus there are two isomeric platinumous chloride diammines $\text{Cl}_2\text{Pt}(\text{NH}_3)_2$ which are both non-electrolytes, as the very feeble conductivity of the aqueous solutions of the two very difficultly soluble compounds shows. The isomer formerly known as platossammine chloride was first obtained by REISET in 1844 by heating dry tetrammine platinumous chloride to 250°. The other isomer, formerly known as platosemidiammine chloride, was obtained

¹⁵ H. BRAUNE and S. KNOKE, *Z. physik. Chem.*, 1933, **B 21**, 297; L. O. BROCKWAY and L. C. PAULING, *Proc. Nat. Acad. Sci., U.S.*, 1933, **19**, 68.

¹⁶ R. V. G. EWENS and M. W. LISTER, *Trans. Faraday Soc.*, 1938, **34**, 1358.

¹⁷ B. GOSSNER and O. KRAUS, *Z. Krist.*, 1934, **88**, 298 (in some cases the wrong structure); likewise L. PASSERINI and M. A. ROLLIER, *Atti R. Accad. Lincei*, 1935, [vi], **21**, 364; L. C. PAULING, *Z. Krist.*, 1935, **91**, 367.

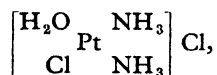
¹⁸ Electron diffraction: L. O. BROCKWAY, R. V. G. EWENS and M. W. LISTER, *Trans. Faraday Soc.*, 1938, **34**, 1350. Cr—C distance 1.92, Mo—C 2.08, W—C 2.06 ± 0.04 Å.

¹⁹ H. BRAUNE and P. PINNOW, *Z. physik. Chem.*, 1937, **B 35**, 239.

^{19a} Tetrahedral structure for $\text{Si}(\text{OC}_2\text{H}_5)_4$ derived from the RAMAN spectrum: J. DUCHESNE, *J. Chem. Phys.*, 1948, **16**, 1009. Cf. H. M. POWELL, D. CLARK and A. F. WELLS, *J. Chem. Soc.*, 1942, p. 642.

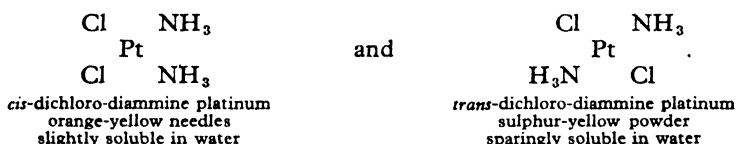
^{19b} Review of the co-ordination theory with respect to the platinum metals: R. GILCHRIST, *Chem. Rev.*, 1943, **32**, 329 ff.

by PEYRONE in 1845 from platinous chloride and ammonia. In aqueous solution, the still more sparingly soluble isomeric form platostammine chloride is slowly formed via chloro-aquo-diammine platinous chloride



the existence of which can be detected by an increase in the conductivity.

WERNER explained the isomerism of the two forms by a planar structure with a different arrangement of the chlorine and the ammonia. By reason of configurational determinations which, it is true, were not unequivocal, he assigned the platosemidiammine chloride the *cis* and the platostammine chloride the *trans* formulation:



For a time, the possibility that the compounds might bear the relationship of polymers to one another was also considered²⁰. But this conjecture was finally proved to be incorrect²¹. It thus proved necessary to accept as correct the explanation of the isomerism by stereoisomerism, as already put forward by WERNER. The supposition of a polymerism was by no means to be rejected at the outset, since a dimer of dichloro-diammine platinum, the dark-green insoluble MAGNUS salt²², was already known. This, according to its formation from tetrammine platinous chloride and potassium chloroplatinite, must be tetrammine platinous chloroplatinite:



A soluble salt, potassium ammino-trichloroplatinite $\text{K} \left[\begin{array}{c} \text{NH}_3 \\ \text{Pt} \\ \text{Cl}_3 \end{array} \right]$ (COSSA's salt), is also formed from K_2PtCl_4 and NH_3 along with the *trans*-dichloro-diammine platinum.

The *cis*-dichloro-diammine platinum dissolves in ammonia with the formation of chloro-triammine platinous chloride $\left[\begin{array}{c} (\text{NH}_3)_3 \\ \text{Pt} \\ \text{Cl} \end{array} \right] \text{Cl}$ and tetrammine platinous chloride $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$. On boiling the latter with hydrochloric acid two molecules of ammonia are split off, whereupon the yellow

²⁰ H. REIHLEN and K. T. NESTLE, *Liebigs Ann. Chem.*, 1926, **447**, 211.

²¹ A. R. HANTZSCH, *Ber.*, 1926, **59**, 2761; A. R. HANTZSCH and F. ROSENBLATT, *Z. anorg. Chem.*, 1930, **187**, 241; A. A. GRÜNBERG, *ibid.*, 1926, **157**, 299; 1927, **164**, 207; *Helv. chim. Acta*, 1931, **14**, 455.

²² There is still another red isomeric form of MAGNUS' salt which must be assigned the same complex formula. The cause of this isomerism is still unknown. S. M. JØRGENSEN and S. P. L. SØRENSEN, *Z. anorg. Chem.*, 1906, **48**, 441; E. HERTEL and K. SCHNEIDER, *ibid.*, 1931, **202**, 77; E. G. COX, F. W. PINKARD, W. WARDLAW and G. H. PRESTON, *J. Chem. Soc.*, 1932, p. 2527; H. D. K. DREW and H. J. TRESS, *ibid.*, 1935, p. 1586.

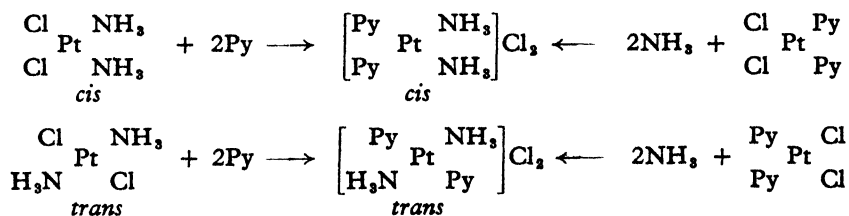
cis-dichloro-diammine platinum is not reformed, and the isomeric *trans* form results.

The same isomerism that occurs with dichloro-diammine platinum is also found in the complexes which platinous chloride forms with tertiary phosphines, arsines and thioethers: $(R_3P)_2PtCl_2$, $(R_3As)_2PtCl_2$ and $(R_2S)_2PtCl_2$. With thioethers, in addition, the dimeric compound corresponding to MAGNUS' salt, the red $[\{(C_2H_5)_2S\}_4Pt]PtCl_4$, is obtained by the action of diethyl sulphide on K_2PtCl_4 , along with the two yellow monomeric forms of $\{(C_2H_5)_2S\}_2PtCl_2$.

Ethylenediamine forms only one compound of the type $enPtCl_2$, since it cannot occupy opposite corners of a planar quadrangle.

Chemical proofs of configuration for all these and similar compounds suffer from the fact that use is made either of the assumption that the new group takes the place of its predecessor, or that neighbouring groups which find themselves directly at the centre of the stereoisomerism react with one another. But since proofs executed by the help of different reactions do not lead to conflicting results, the conclusiveness assigned to them in their totality is not to be too lowly esteemed. In individual cases it has been possible to fix the configuration quite independently of them by physical means. So far the results have been in agreement with those obtained by chemical methods.

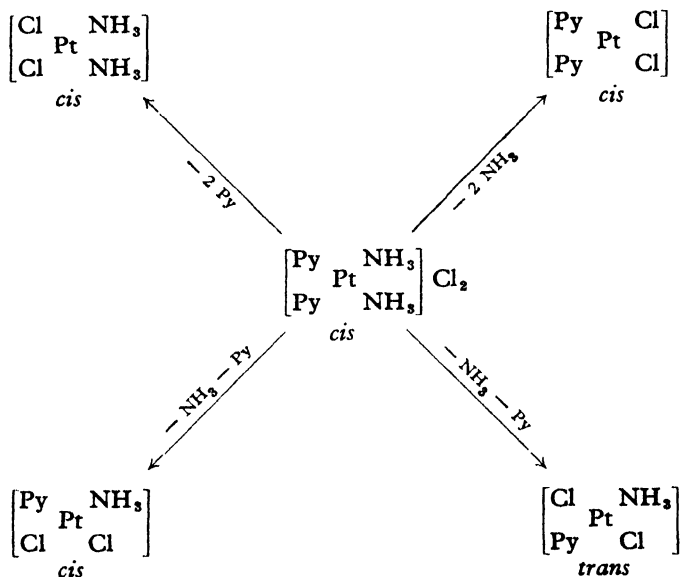
The first proof WERNER employed utilized the conversion by pyridine of the two isomeric non-electrolytes $Cl_2Pt(NH_3)_2$ into the isomeric salts $[Py_2Pt(NH_3)_2]Cl_2$ and their reconversion into non-electrolytes. Platosammine chloride thereupon remains in the same steric series. The expulsion of the chlorine from the first into the outer sphere proceeds in a steric sense completely uniformly. The two diammine-dipyridino chlorides are in fact obtained from Cl_2PtPy_2 and ammonia as well as from $Cl_2Pt(NH_3)_2$ and pyridine. If one assumes that the molecules entering in place of the chlorine take up the position of the latter, that is, that the configuration is conserved, the following formulae result:



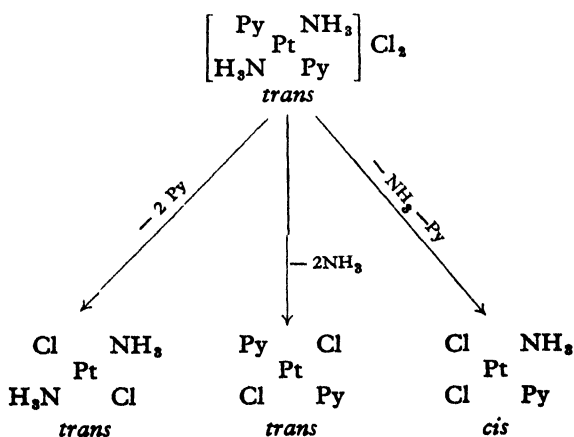
From one of the two isomeric salts $[Py_2Pt(NH_3)_2]Cl_2$, hydrochloric acid extracts one ammonia and one pyridine molecule, and from the other either two ammonia or two pyridine molecules. In the one case a single product of reaction is obtained, a mixed non-electrolyte, in the other two unmixed non-electrolytes side by side. The latter possess the configuration of the starting material. For the mixed non-electrolytes, a conclusive configura-

tional proof is lacking. WERNER assumes for these a configuration differing from that of the starting material.

In considering the formula of the *cis-trans* isomeric salts $[(\text{NH}_3)_2\text{PtPy}_2]\text{Cl}_2$, it is perceived that by cleavage of the *cis* form with the preservation of the configuration three compounds can arise, according to whether 2NH_3 , $2\text{C}_5\text{H}_5\text{N}$ or $\text{NH}_3 + \text{C}_5\text{H}_5\text{N}$ are split off from *cis* positions. With change in the configuration, on the other hand, only one option is possible, this leading to the mixed *trans* non-electrolyte:



From the *trans* form, by contrast, with the preservation of the configuration only two compounds result by splitting off either two molecules of ammonia or two of pyridine. The loss of one molecule of each leads here with change in configuration to the mixed *cis* compound:



In all these considerations, it is presupposed that the chlorine atoms take up the positions of the groups they displace on substitution.

Because the cleavage product of platosemidiammine chloride is a mixed one and is effected with change in configuration, while from platosammine chloride only the two uniform cleavage reactions occur with retention of the configuration, WERNER believed himself obliged to assign the former the *cis* and the latter the *trans* formulation. This conclusion thus combines the number of parallel competing reactions observed with the number of possibilities of preservation or non-preservation of the configuration. With the *cis* form these possibilities are 3 and 1, with the *trans* form 2 and 1. If these are now combined with the number of the observed reactions, one of the uniform reactions must always occur with non-preservation of the configuration. Since in the second case only two and not three reactions were observed, this corresponds to the *trans* form.

There is, however, absolutely no reason for agreeing with the validity of this combination postulated by WERNER. It is manifest that he either held it for self-evident, or was not at all clear concerning the ways and means he used here to combine different things with one another, since he does not examine the suppositions which form the foundation of his deductions. On the basis of the previously mentioned reflections, an unbiased person would expect four competing reactions with the *cis* form and three with the *trans* form, and a corresponding number of reaction products. But since their number is smaller, the possibilities of substitution must be limited by a definite principle, as is also the case in the directive substitution of the benzene ring. If it is assumed that the chlorine always chooses two positions opposite to one another and never two neighbouring places, so that consequently *trans* non-electrolytes always result from the $[(\text{NH}_3)_2\text{PtPy}_2]^{+}$ ion, agreement with observation is obtained. In this way one arrives at the identical configuration assumed by WERNER. Admittedly, use is made of an improved postulate, namely that of *trans* substitution by chlorine, but the by no means justifiable, arbitrary combinations of WERNER are avoided²³.

WERNER's second proof is less vulnerable. It rests on the relationships of the two isomeric diammine platinous chlorides to the octahedrally constructed platonic compounds, whose configuration can be proved with certainty. With chlorine, platosemidiammine chloride gives the *cis*- and platosammine chloride the *trans*-tetrachloro-diammine platinum $[\text{Cl}_4\text{Pt}(\text{NH}_3)_2]$ (see Fig. 7).

The platinous non-electrolytes must have the same configuration as the platonic non-electrolytes, provided that no interchange of positions among the groups occurs with the approach of the chlorine.

²³ Upon what WERNER's manner of proof really rests has nowhere been explained until now. The proof given by him is everywhere accepted without comment. It is for this reason that it has been gone into so closely here, although it is really no proof.

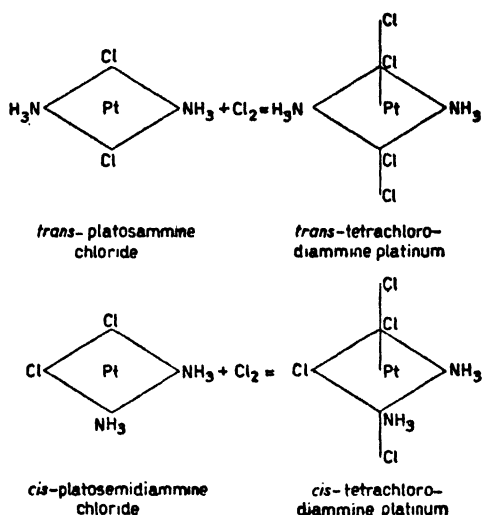
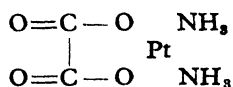


Fig. 7. Configurational proof for diammine platinous chloride by the addition of chlorine to form *cis*- and *trans*-platonic compounds.

As with the co-ordination number 6, the *cis* configuration can be proved by substitution of two *cis*-orientated groups by one which occupies two co-ordination positions. Upon this rest two lines of proof by DREW, WARDLAW and co-workers²⁴.

(i) If, with the help of silver oxide, the chlorine in *cis*-dichloro-diammine platinum is replaced by hydroxo groups, the dihydroxo-compound thus obtained is able to form an oxalato-compound

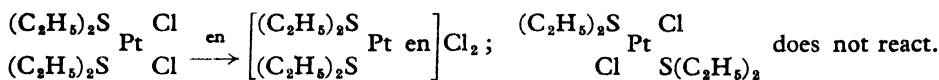


with oxalic acid, whereas the dihydroxo-compound from the isomeric *trans* form is not able to. Hydrochloric acid converts the hydroxo-compound back into the original dichloro-compound.

(ii) *Cis*-dichloro-diammine platinum, but not *trans*-, reacts with ethylenediamine to form [en₂Pt(NH₃)₂]Cl₂. An analogous proof has been supplied for the *cis-trans* isomeric thioether-compounds²⁵:

²⁴ H. D. K. DREW, F. W. PINKARD, W. WARDLAW and E. G. COX, *J. Chem. Soc.*, 1932, p. 988. Non-existence of the third isomeric chloride described here: F. ROSENBLATT and A. SCHLEEDER, *Ber.*, 1933, 66, 472; K. A. JENSEN, *Z. anorg. Chem.*, 1936, 229, 252. Yet a third proof: F. W. PINKARD, H. SAENGER and W. WARDLAW, *J. Chem. Soc.*, 1933, p. 1056.

²⁵ Isomerism of the thioether-complexes: C. W. BLOMSTRAND, *J. prakt. Chem.*, 1888, [ii], 38, 352; L. TSCHUGAIEFF, *Z. anorg. Chem.*, 1913, 82, 420; H. D. K. DREW, G. H. PRESTON, W. WARDLAW and G. H. WYATT, *J. Chem. Soc.*, 1933, p. 1294; E. G. COX, H. SAENGER and W. WARDLAW, *ibid.*, 1934, p. 182; H. D. K. DREW and G. H. WYATT, *ibid.*, 1934, p. 56; K. A. JENSEN, *Z. anorg. Chem.*, 1935, 225, 97; 115.



Independent of these chemical proofs are the determinations of configuration by physical means. A direct insight into the spatial structure is afforded by X-ray analysis, which, however, has been carried out for only a few compounds belonging to this class. In this manner, a planar structure for the PtCl_4 '' complex²⁶ has been demonstrated in potassium tetrachloroplatinite $\text{K}_2[\text{PtCl}_4]$, and a planar structure for the $\text{Pt}(\text{NH}_3)_4$ '' complex²⁷ in tetrammine platinous chloride $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$. Also in the green MAGNUS salt, which is constructed from these two complexes, the latter are planar. The same holds true for its red isomer, which possesses a slightly different crystal structure²⁸. A corresponding direct proof for the isomeric diammine-complexes has not yet been provided. Only in the case of the analogously built *cis-trans* isomeric dinitro-diammine-palladous complexes $(\text{NH}_3)_2\text{Pd}(\text{NO}_2)_2$ has the configuration been proved by X-ray analysis²⁹ and a dissimilarity ascertained with respect to the salt $[\text{Pd}(\text{NH}_3)_4][\text{Pd}(\text{NO}_2)_4]$.

With the platinum complexes, a further X-ray analytical proof is available for the stereoisomerism of the thioether-complexes. The difficultly soluble complex, which does not react with ethylenediamine, possesses, according to the X-ray analysis³⁰, a plane of symmetry perpendicular to a two-fold axis. This is possible only for a *trans* arrangement of the groups. For the isomeric *cis* compound, it is true, a planar *cis* arrangement cannot be derived from the X-ray pattern. Nevertheless, the latter indicates that the symmetry of the complex is lower than that of the *trans* compound.

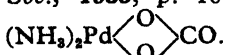
A further physical proof for the planar configuration of the *trans* compound is possible by means of dipole measurement. Planarly built *trans* compounds, since they possess a centre of symmetry, like *trans*-ethylene derivatives or *para*-substituted benzene derivatives with identical substituents, may not possess a dipole moment if the groups possess a rotational symmetry. One form of the tertiary-phosphine- and tertiary-arsine-complexes, $(\text{R}_3\text{P})_2\text{PtCl}_2$ and $(\text{R}_3\text{As})_2\text{PtCl}_2$ respectively, is indeed without a dipole moment, while the other possesses a large moment³¹. With the thioether-complexes, this manner of proof is not applicable on account of the angular configuration of the substituents on the sulphur, which also for the *trans* compounds

²⁶ R. G. DICKINSON, *J. Am. Chem. Soc.*, 1922, **44**, 774; 2404.

²⁷ E. G. COX, *J. Chem. Soc.*, 1932, p. 1912; E. G. COX, F. W. PINKARD, W. WARDLAW and G. H. PRESTON, *ibid.*, p. 2527; E. G. COX and G. H. PRESTON, *ibid.*, 1933, p. 1089.

²⁸ E. HERTEL and K. SCHNEIDER, *Z. anorg. Chem.*, 1931, **202**, 77.

²⁹ F. G. MANN, D. M. CROWFOOT, D. C. GATTIKER and N. WOOSTER, *J. Chem. Soc.*, 1935, p. 1642. Here also the *cis* configuration has been proved by

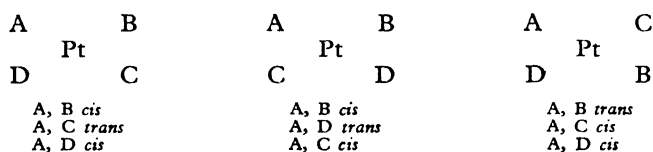


³⁰ E. G. COX, H. SAENGER and W. WARDLAW, *J. Chem. Soc.*, 1934, p. 182.

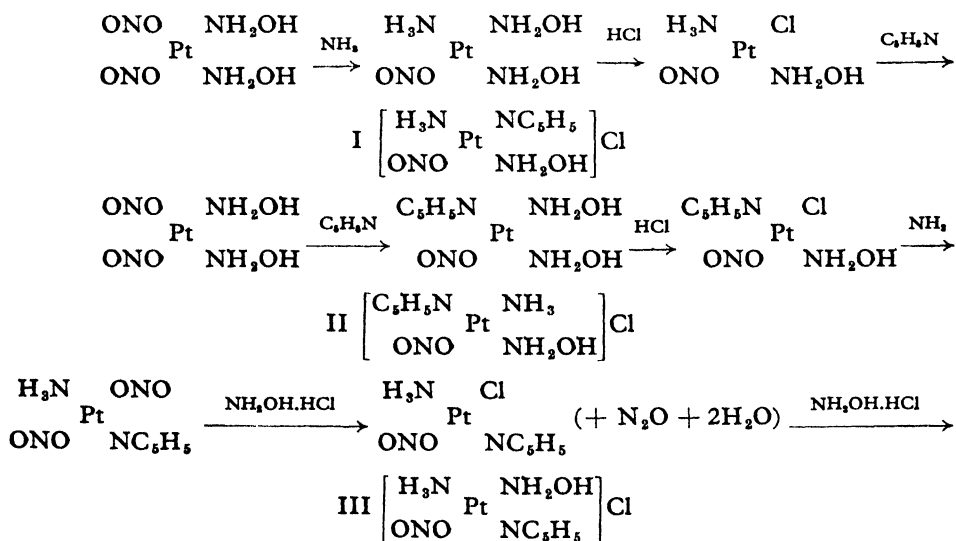
³¹ K. A. JENSEN, *Z. anorg. Chem.*, 1936, **229**, 225.

may stipulate a dipole moment, as in the case of bent substituents in the *para* configuration on the benzene ring.

The proof of a planar arrangement of the four groups in platinous complexes can also be carried out with compounds which possess four different substituents. With the tetrahedral arrangement there must be two mirror-image, optically active forms: with a planar arrangement, on the other hand, three isomers:



TSCHERNIAEV³² found this in the case of ammine-hydroxylamino-pyridino-nitrito platinous chloride. His method of proof, in which he subjected *cis*-dihydroxylamino-dinitrito platinum $(\text{NH}_2\text{OH})_2\text{Pt}(\text{ONO})_2$ and dinitrito-pyridino-ammine platinum $(\text{NH}_3)\text{PyPt}(\text{ONO})_2$ to various reactions, is illustrated by the following formulae (it being assumed thereby for the sake of simplicity that the new group takes the place of its predecessor, although this assumption is without consequence for the conclusiveness of the experiments, which depends only upon the number (3) of the isomers prepared):



The same planar structure as in the complex platinum and palladium compounds occurs again in the crystal lattice of palladous chloride³³, which may be regarded as the "autocomplex" compound $\text{Pd}[\text{PdCl}_4]$ ³⁴. The lattice

³² I. I. TSCHERNIAEV, *Ann. Inst. Platine (U.S.S.R.)*, 1928, 6, 55 (= *Chem. Centr.*, 1929 I, p. 1204). In the abstract the proof is scarcely evident. For simplicity it is formulated here as the chloride, whereas TSCHERNIAEV prepared the chloroplatinite $[\text{Py}(\text{NH}_3)(\text{ONO})(\text{NH}_2\text{OH})\text{Pt}]_2\text{PtCl}_4$.

³³ A. F. WELLS, *Z. Krist.*, 1938, 100, 189.

³⁴ For further concerning crystalline autocomplexes, see Chapter VII, 3, (iv).

contains planar, though certainly not quite square, PdCl_4 groups arranged in an unending chain, each group possessing two chlorine atoms in common with the next ³⁶.

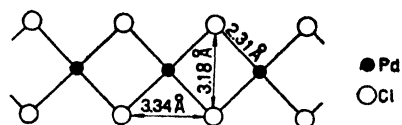
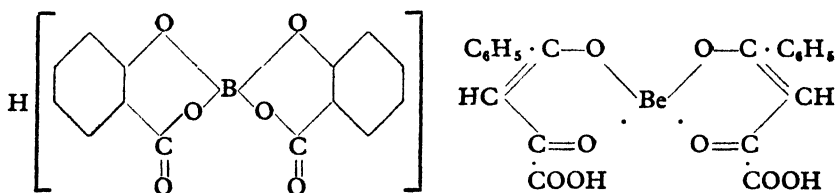


Fig. 8. Chain from the lattice of palladous chloride. The $\text{Pd} \begin{array}{c} \diagup \text{Cl} \\ \diagdown \text{Cl} \end{array} \text{Pd}$ quadrilateral is not quite rectangular, but is rhombic with an angle of 87° . The chains lie in the rhombic lattice parallel to the b axis. Their planes lie in two different directions perpendicular to one another, which differ from the directions of the a and c axes.

It has been necessary to draw on the physical method of structure analysis by X-rays for all compounds with the co-ordination number 4 not derived from divalent platinum or palladium, so far almost without exception, in order to decide whether the configuration is planar or tetrahedral. Exceptions to these are the tetrahedrally constructed inner complexes of certain elements with organic compounds of the spirane type which, in consequence of their molecular symmetry, have been resolved into optical antipodes or enantiomorphs, as, for example, borosalicylic acid ³⁶ or the complexes of the enolized form of benzoylpyruvic acid with beryllium and zinc ³⁷.



Then there are also inner-complex salts which, in consequence of the peculiarity of the atomic framework in which the central atom is anchored, must have a *planar* construction, like the chlorophyll-complex of magnesium, the haemin-complex of iron and the phthalocyanine-complexes of copper and other metals.

With the help of X-ray structure analysis, *planar* configurations have been ascertained for the following: complexes of divalent copper, $\text{Cu}(\text{OH}_2)_4$ ³⁸ $\text{Cu}(\text{NH}_3)_4$ ³⁹ and $\text{Cu}(\text{CN})_4$ ⁴⁰; complexes of divalent palladium and platinum, $\text{Pd}(\text{NH}_3)_4$ ³⁹, $\text{Pd}(\text{CN})_4$ ⁴⁰ and $\text{Pt}(\text{CN})_4$ ⁴⁰; complexes of diva-

³⁶ Comprehensive review of square complexes: D. P. MELLOR, *Chem. Rev.* 1943, **33**, 137.

³⁷ J. BÖESEKEN and J. MEULENHOF, *Proc. K. Acad. Wetensch. Amsterdam*, 1924, **27**, 174.

³⁸ W. H. MILLS and R. A. GOTTS, *J. Chem. Soc.*, 1926, p. 3121.

³⁹ C. A. BEEVERS and H. LIPSON, *Proc. Roy. Soc.*, 1934, **A 146**, 570.

⁴⁰ Other complexes of divalent copper: E. G. COX and K. C. WEBSTER, *J. Chem. Soc.*, 1935, p. 731; E. G. COX, W. WARDLAW and K. C. WEBSTER, *ibid.*, 1936, p. 775.

⁴¹ B. N. DICKINSON, *Z. Krist.*, 1934, **88**, 281.

lent nickel, $\text{Ni}(\text{CN})_4''$ ⁴¹ and nickel dimethylglyoxime⁴² among others⁴³; complexes of divalent silver⁴⁴; complexes of trivalent gold, AuCl_4' ⁴⁵, AuBr_4' ; and ICl_4' in potassium tetrachloriodide KICl_4 ⁴⁶.

The following are *tetrahedrally* constructed: complexes of monovalent copper, such as $\text{Cu}(\text{CN})_4'''$ ⁴⁷; the aurocyanide ion $\text{Au}(\text{CN})_4'''$; complexes of zinc and cadmium, $\text{Zn}(\text{CN})_4''$ and $\text{Cd}(\text{CN})_4''$; the oxy-acid anions ClO_4' , MnO_4' , SO_4'' , CrO_4'' , PO_4''' , $\text{CrO}_3\text{F}'$ and $\text{OsO}_3\text{N}'$ ⁴⁸, among others; anions of fluo-acids, BF_4' and BeF_4'' ; HgCl_4'' — $[\text{N}(\text{CH}_3)_4]_2\text{HgCl}_4$ is isomorphous with K_2SO_4 and K_2BeF_4 ⁴⁹ — and CoCl_4'' ; the first-order compounds PtCl_4 , trimethyl-chloro platinum $(\text{CH}_3)_3\text{PtCl}$ ⁵⁰ and nickel tetracarbonyl $\text{Ni}(\text{CO})_4$ ⁵¹.

It follows from the last-named examples, as also from the examples of the copper complexes, that the planar or tetrahedral arrangement about the central atom is not stipulated simply by its chemical nature, but that the configuration also depends on its valency. Thus divalent platinum has a planar and tetravalent a tetrahedral configuration, while that of copper is planar when it is divalent and tetrahedral when monovalent. But under certain circumstances the configuration can also be different for the same valency. Thus the ion CoCl_4'' , derived from divalent cobalt, is tetrahedral⁵² in the salt $\text{Cs}_3\text{CoCl}_5 = \text{Cs}_2\text{CoCl}_4 \cdot \text{CsCl}$ and in the isomorphous Rb_3CoCl_5 , whereas in dichloro-dipyridino cobalt $(\text{C}_5\text{H}_5\text{N})_2\text{CoCl}_2$, of which there is yet another

⁴¹ Barium salts with $4\text{H}_2\text{O}$: H. BRASSEUR and A. DE RASSENFOSSE, *Bull. soc. franç. minéral.*, 1938, **61**, 129.

⁴² Here, with the unsymmetrical nickel methylbenzylglyoxime, two isomers are known which are apparently *cis-trans* isomers: S. SUGDEN, *J. Chem. Soc.*, 1932, p. 246. The same also seems to hold for the two isomeric nickel methylglyoximes found by L. TSCHUGAIEFF, *J. Russ. Phys. Chem. Soc.*, 1910, **42**, 1466 (= *Chem. Centr.*, 1911 **I**, p. 871).

⁴³ *E.g.*, the dithio-oxalate and salicylaldoxime compounds among others: E. G. COX, F. W. PINKARD, W. WARDLAW and K. C. WEBSTER, *J. Chem. Soc.*, 1935, p. 459; E. G. COX, W. WARDLAW and K. C. WEBSTER, *ibid.*, p. 1475.

⁴⁴ E. G. COX and K. C. WEBSTER, *J. Chem. Soc.*, 1935, p. 731; E. G. COX, W. WARDLAW and K. C. WEBSTER, *ibid.*, 1936, p. 775.

⁴⁵ E. G. COX and K. C. WEBSTER, *J. Chem. Soc.*, 1936, p. 1635.

⁴⁶ R. C. L. MOONEY, *Z. Krist.*, 1938, **98**, 377. The four Cl atoms form a somewhat deformed square. KICl_4 is prepared from an almost saturated KCl solution, iodine and much chlorine.

⁴⁷ E. G. COX, W. WARDLAW and K. C. WEBSTER, *J. Chem. Soc.*, 1936, p. 775.

⁴⁸ F. M. JAEGER and J. E. ZANSTRA, *Proc. K. Acad. Wetensch. Amsterdam*, 1932, **35**, 610; 779; 787. *Rec. trav. chim. Pays-Bas*, 1932, **51**, 1013. Potassium osmiumate KOsO_3N with octavalent osmium is prepared from OsO_4 , KOH and concentrated ammonia at 40° as lemon-yellow, tetragonal prisms. The Rb, Cs, NH_4 and TI^{I} salts are rhombic pseudo-tetragonal.

⁴⁹ T. V. BARKER, *J. Chem. Soc.*, 1912, **101**, 2488.

⁵⁰ E. G. COX and K. C. WEBSTER, *Z. Krist.*, 1935, **90**, 561. In the lattice $(\text{CH}_3)_3\text{PtCl}$ and $\text{Pt}(\text{CH}_3)_4$ are tetrameric (p. 150).

⁵¹ B. L. CRAWFORD (Jr) and P. C. CROSS, *J. Chem. Phys.*, 1938, **6**, 525. (From the vibration spectrum, RAMAN effect and diffraction of electrons.) A tetrahedron for $\text{Ni}(\text{CO})_4$ has also been proved by recent RAMAN-spectrum measurements: B. L. CRAWFORD (Jr) and W. HORWITZ, *ibid.*, 1948, **16**, 147. The data in *ibid.*, 1934, **2**, 636, are incorrect.

⁵² H. M. POWELL and A. F. WELLS, *J. Chem. Soc.*, 1935, p. 359.

isomer (*cis-trans* isomerism??)⁵³, the groups lie in a plane⁵⁴, although it is also derived from divalent cobalt. For the salt $(\text{NH}_4)_3\text{ZnCl}_5 = (\text{NH}_4)_2\text{ZnCl}_4 \cdot \text{NH}_4\text{Cl}$, the relationships are exactly the same as for Cs_3CoCl_5 ⁵⁵.

A pyramidal structure for complexes in which the central atom has the co-ordination number 4 is not so far known, nor has it been demonstrated for compounds of the first order. Nevertheless, it is not in consequence excluded, that such a structure will eventually come under observation (cf. Chapter VII, 3, (iii)).

It cannot be stated which causes are to be made responsible for the planar structure in some, and the tetrahedral in other complexes, without a further knowledge of the distribution of the valence electrons when the bonds between the central atom and the groups come into existence. A knowledge of this is not needed for the systematization of complex compounds, since the planar or tetrahedral structure is accepted as an experimental fact. As a consequence, this question will first be gone into more closely on arriving at the point where the bonding relationships will be discussed.

On the other hand, there is yet another point to be critically examined, namely the question of how far the co-ordination number can be unequivocally derived from the stoichiometric composition of a compound. The answer is a prerequisite to the discussion of the spatial structure of complexes. In his derivation of the configuration of the isomeric planar platinum complexes, WERNER proceeded from the assumption that the compound corresponding to the formula $\text{Cl}_2\text{Pt}(\text{NH}_3)_2$ was mononuclear, and that in it platinum must possess the co-ordination number 4, since a non-electrolyte was under discussion. The fact that this assumption, which is now known to be correct, could have been disputed, inasmuch as there was a desire to see the isomerism explained by a polymerism, proves that it is not self-evident. Precisely in the cases of the difficultly soluble non-electrolytes, for which no reliable determinations of the molecular weight are possible, the question must be asked whether the complexes are present in the crystal as an association of independent units, or whether several or even infinitely many complexes are bound together in the lattice in accordance with the principle of polynuclear complex compounds. The classical co-ordination theory of WERNER had often enough to leave open this question which, moreover, was frequently passed over with too little heed. Today it can be unequivocally answered in the majority of cases with the help of X-ray structure analysis. How difficult the respective relationships can be on occasions, and how carefully one must guard against conclusions by analogy which present themselves as really obvious, will next be discussed for examples in which the compounds possess the same formal composition as dichloro-diammine platinum. Of the numerous substances with this composition,

⁵³ E. D. P. BARKWORTH and S. SUGDEN, *Nature*, 1937, **139**, 374.

⁵⁴ E. G. COX, A. J. SHORTER, W. WARDLAW and W. J. R. WAY, *J. Chem. Soc.*, 1937, p. 1556.

⁵⁵ H. P. KLUG and L. ALEXANDER, *J. Am. Chem. Soc.*, 1944, **66**, 1056.

the following will be selected: $\text{Cl}_2\text{Pt}(\text{NH}_3)_2$, $\text{Cl}_2\text{Zn}(\text{NH}_3)_2$, $\text{Cl}_2\text{Cd}(\text{NH}_3)_2$ and $\text{Cl}_2\text{Hg}(\text{NH}_3)_2$.

The question to be answered first is whether non-electrolytes are under discussion or salts of the type $[\text{M}^{\text{II}}(\text{NH}_3)_2]\text{Cl}_2$, in which the metal has the co-ordination number 2 like silver in diammine silver chloride $[\text{Ag}(\text{NH}_3)_2]\text{Cl}$. It is not always so easy to answer as in the case of the platinum compounds. Difficulties arise if the compounds prepared from aqueous solutions of the chlorides and excess ammonia and ammonium chloride react in some way with pure water, so that ion-forming salts result in part from the non-electrolytes. Since this is the case for various compounds of this type, other criteria have been sought without, it is true, ever being able to settle the question unequivocally with their help. By way of example, the isothermal decomposition of the hexammines speaks for assigning a special nature to the diammines⁵⁶, this leading without observable intermediate stages to the diammine, whose stability is given by its small dissociation pressure of ammonia. Thus for $\text{Fe}(\text{NH}_3)_n\text{Br}_2$, for example, the isotherms at 107° and 230° appear as shown in Fig. 9. At 107° and pressures of ammonia below 120 mm,

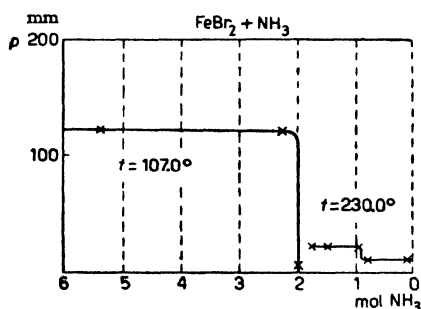


Fig. 9. Vapour-pressure isotherms for the ammoniates of ferrous bromide

the diammine is practically completely stable. Only at 230° does the vapour pressure of ammonia attain the value of about 20 mm. Below this pressure it is converted with the release of ammonia to the monammine, which is in equilibrium with ammonia-free FeBr_2 at a pressure only slightly lower. Even if this singular position of the diammine with its broad region of existence suggests a connection with its special constitution, namely that of a non-electrolyte, it is nevertheless no certain proof for it.

Now in the case of the four diammines already cited, X-ray analyses have shown with certainty that they are non-electrolytes. The lattices of the compounds contain no chloride ions. But quite considerable differences exist in their structures which, from the standpoint of the classical co-ordination theory, appear to be surprising.

In $\text{Cl}_2\text{Pt}(\text{NH}_3)_2$, platinum has the co-ordination number 4 and chlorine

⁵⁶ There are numerous papers concerning this by W. BILTZ. Résumé: *Z. anorg. Chem.*, 1923, 130, 93.

the co-ordination number 1, the complex being planar and discrete in the lattice ⁵⁷.

In $\text{Cl}_2\text{Zn}(\text{NH}_3)_2$, zinc likewise possesses the co-ordination number 4 and chlorine the co-ordination number 1, the complex here being tetrahedral and having an independent existence as a molecule ⁵⁸ (Fig. 10).

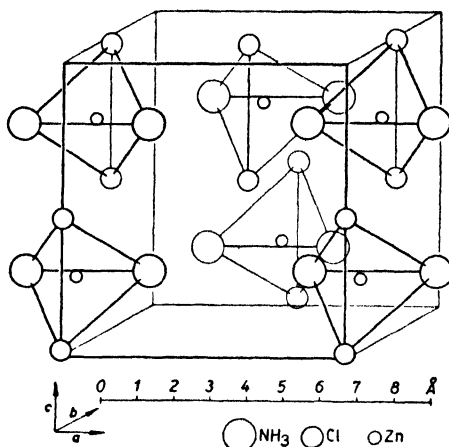


Fig. 10. Lattice of $\text{Zn}(\text{NH}_3)_2\text{Cl}_2$

In $\text{Cl}_2\text{Cd}(\text{NH}_3)_2$, cadmium has the co-ordination number 6 and chlorine the co-ordination number 2, the complex being octahedral with the two ammino groups in the axial configuration ⁵⁹ (Fig. 11). Each octahedron has two edges formed by chlorine atoms common with two neighbours, as is the case in the polynuclear compounds containing halogen bridges (pp. 168, 172). In the direction of the crystallographic c axis, infinite chains of octahedra linked to each other in this manner align themselves according to the scheme illustrated in projection on the left of Fig. 11. The dotted lines indicate the manner in which the $\text{Cl}_2\text{Cd}(\text{NH}_3)_2$ molecules, which are not capable of independent existence, align themselves in the lattice, and illustrate how the empirical formula $\text{Cl}_2\text{Cd}(\text{NH}_3)_2$ is provided by this kind of linking ⁶⁰.

The lattice of $\text{Cl}_2\text{Hg}(\text{NH}_3)_2$ is again constructed quite differently ⁶⁰, but it would lead too far afield to examine it more closely here.

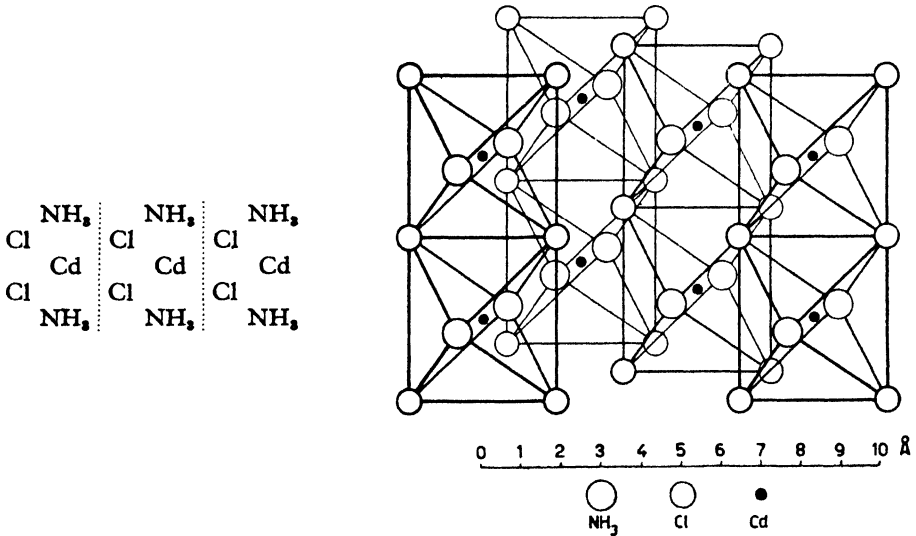
For complex compounds which are known in the crystalline state, the empirical formula indicating the co-ordination number 4 consequently pronounces nothing with certainty concerning the co-ordination number in the lattice. Let this be illustrated further by a few additional examples of anionic complexes. Thus, as might be expected, in the BF_4^- ion, which is

⁵⁷ The proof has so far been adduced only for the analogous palladium compound $(\text{NH}_3)_4\text{Pd}(\text{NO}_2)_2$ (p. 116).

⁵⁸ C. H. MACGILLAVRY and J. M. BIJVOET, *Z. Krist.*, 1936, **94**, 249.

⁵⁹ C. H. MACGILLAVRY and J. M. BIJVOET, *Z. Krist.*, 1936, **94**, 231.

⁶⁰ The structure is related to that of cupric chloride dihydrate = dichloro-diaquo copper (p. 137).

Fig. 11. Lattice of $\text{Cd}(\text{NH}_3)_2\text{Cl}_2$

known to be tetrahedral in crystals as well as in solution, boron possesses the co-ordination number 4. On the other hand, the salt TlAlF_6 does *not* contain the AlF_4' complex. Rather, the aluminium has here the co-ordination number 6 with an AlF_6 octahedron, such as is familiar in cryolite and other complex aluminium fluorides, situated at the centre of a tetragonal prism, at the corners of which are eight thalious ions, these in turn being surrounded by eight fluorine atoms from different AlF_6''' complexes. The fluorine

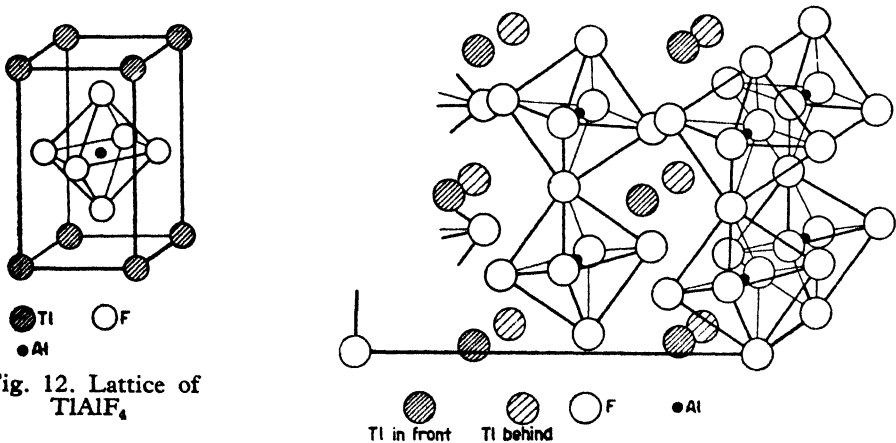
Fig. 12. Lattice of TlAlF_6

Fig. 13. Lattice of Tl_3AlF_6 . The directions of the rhombic axes are indicated at the fluorine atoms at the lower right-hand and left-hand corners. The dimensions of the elementary unit are given by the distance between these two atoms and the height of the figure. The contact of two octahedra by a corner is to be seen especially clearly in the middle of the diagram. Their fourfold axes form an obtuse angle with one another (differing from that in Fig. 22, p. 154).

atoms are situated at an appreciably greater distance from the thallium than from the aluminium⁶¹ (Fig. 12).

In the complex salt Tl_2AlF_6 , the co-ordination number of aluminium is similarly 6 and not 5. Here the AlF_6 octahedra form an unending chain, being linked together by means of a fluorine atom at a corner, with the thalious ions arranged in between (Fig. 13). The Al—F distance, 1.91 Å, is incidentally appreciably greater here than for the AlF_6''' complex in the salt $TlAlF_4$, where it is 1.80 Å⁶².

Another example is potassium mercurichloride $K_2HgCl_4 \cdot H_2O$. Here also the central atom has the co-ordination number 6 and not 4, and there are no isolated $HgCl_4''$ ions in the lattice, otherwise than for $[N(CH_3)_4][HgCl_4]$ (p. 119). The lattice structure⁶³ is completely different from that of $TlAlF_4$. The mercury is surrounded pseudo-octahedrally by six chlorine atoms. Each deformed octahedron is fused with two others of the same kind along two of its edges. With these others it has two chlorine atoms in common,

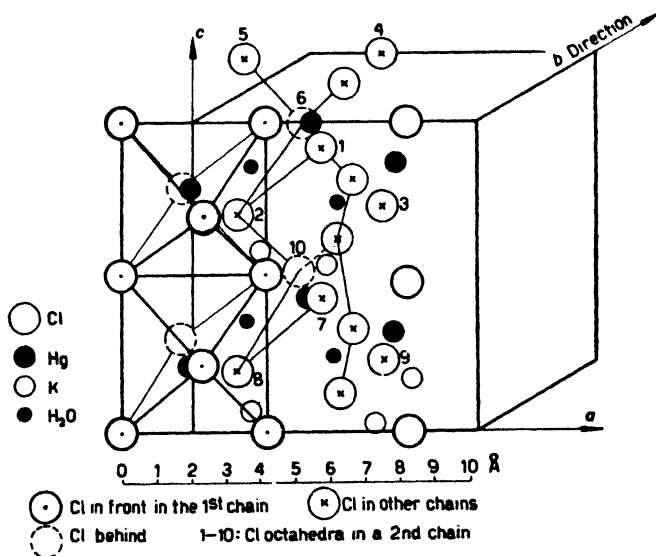


Fig. 14. Lattice of potassium mercurichloride $K_2HgCl_4 \cdot H_2O$. The rhombic elementary unit is indicated in the section. The co-ordination octahedra belonging to the chromate type are joined in pairs by an edge and made identifiable on one occasion by dots and on the other by crosses in the middle of large circles. The octahedra can best be seen on the left-hand side of the diagram. In the lower one, the mercury atom in the centre is almost hidden. The joined octahedra are to be thought of as unending chains continued in the direction of the c axis. The octahedra are really pseudo-octahedra. Each pair of Cl atoms is removed by 2.42, 2.81 and 3.16 Å from the central mercury. Consequently $HgCl_2$ molecules arise in a kind of way in the lattice structure perpendicular to the chain direction (Hg on the left in the diagram with the Cl atom indicated by a dotted circle lying behind the c axis and that indicated by a full circle lying in front of the c axis).

⁶¹ C. BROSSET, *Z. anorg. Chem.*, 1937, **235**, 139. Similarly the alkali salts: *ibid.*, 1938, **239**, 301.

⁶² C. H. MACGILLAVRY, J. H. DE WILDE and J. M. BIJVOET, *Z. Krist.*, 1938, **100**, 212.

⁶³ H. BRASSEUR and A. DE RASSENFOSSE, *Z. Krist.*, 1936, **95**, 474.

so that unending HgCl_4'' chains penetrate the lattice. The chains are held together by the potassium ions, between which the water molecules are arranged (Fig. 14).

With the co-ordination number 3, cases of this sort, in which the co-ordination number in the lattice does not coincide with the apparent co-ordination number of the formula, are more frequent (cf. pp. 127—128).

How little can in general be said about the connection between the co-ordination numbers of the central atom of a complex in the lattice, in the formula and in solution is shown by the example of barium cadmium chloride $\text{Ba}[\text{CdCl}_4].4\text{H}_2\text{O}$ ⁶³. This salt is constructed like barium platinocyanide $\text{Ba}[\text{Pt}(\text{CN})_4].4\text{H}_2\text{O}$ ⁶⁴, thus containing the isolated CdCl_4'' complex in contrast to in the lattice of $\text{K}_2\text{HgCl}_4.\text{H}_2\text{O}$, which does not contain the HgCl_4'' complex, and to the cadmium chloride complexes with the co-ordination number 3 in $\text{Cs}[\text{CdCl}_3]$ and $\text{NH}_4[\text{CdCl}_3]$ (p. 129). A structural decision is thus always reserved for X-ray analysis.

(iii) Co-ordination Number 3

The spatial structure of compounds of the first order and of complexes with the co-ordination number 3 has been investigated exclusively by physical methods, there being no isomerism to permit the drawing of conclusions with respect to this among inorganic compounds. There are both planar and pyramidal structures to consider. For three similar groups, a planar structure can be proved by the absence and a pyramidal structure by the presence of a dipole moment.

Of the first-order compounds, the halides of boron, BF_3 , BCl_3 and BBr_3 ⁶⁵, do not possess dipole moments and thus have a planar structure; dipole moments and consequently pyramidal structures are possessed by the trihalides of phosphorus, arsenic and antimony, as well as by the hydrides of these elements and by ammonia. The conclusions drawn from the absence or presence of a dipole moment are confirmed by electron diffraction. By X-ray analysis, a planar structure has been proved with certainty for the carbonate ion CO_3'' as well as for the nitrate ion NO_3' and the borate ion BO_3''' . In the chlorate ion ClO_3' and bromate ion BrO_3' , on the contrary, the atoms form a flat pyramid with the halogen atom at the apex. The spatial structures of halo-complexes like CuCl_3' and cyano-complexes like $\text{Cu}^{\text{I}}(\text{CN})_3''$, which incidentally is less stable than the complex $\text{Cu}^{\text{I}}(\text{CN})_4'''$, have not yet been investigated.

The molecules of the non-planar compounds of the first order with the co-ordination number 3 form flat pyramids throughout. The following substances are cited as examples :

⁶⁴ H. BRASSEUR and A. DE RASSENFOSSE, *Bull. soc. franç. minéral.*, 1938, **61**, 129.

⁶⁵ H. A. LÉVY and L. O. BROCKWAY, *J. Am. Chem. Soc.*, 1937, **59**, 2085 (electron diffraction).

molecule XY_3	X—Y distance (Å)	Y—X—Y angle ⁶⁶	dipole moment $\times 10^{18}$
PF_3 ⁶⁷	1.47	110°	?
PCl_3 ⁶⁷	1.98	102°	0.85
PBr_3 ⁶⁸	2.23	100°	0.61
PI_3	2.38	100°	0 ?? *
AsF_3 ⁶⁷	1.70	?	2.65
$AsCl_3$ ⁶⁷	2.13	107°	2.06
$AsBr_3$ ⁶⁸	2.31	101.5°	1.60
AsI_3 ⁶⁸	2.51	102.5°	0.96
SbF_3 ⁶⁹	2.0	?	?
$SbCl_3$	2.37	104°	3.2
$SbBr_3$ ⁶⁸	2.47	98°	~2.9
SbI_3 ⁶⁸	2.70	90°	1.5
NH_3	1.02	109°	1.46
PH_3 ⁷⁰	1.46	99°	0.55
AsH_3 ⁷⁰	1.56	97°	0.16

* See p. 416, footnote 16.

According to experience gained so far, a simple rule can be given which states whether a molecule or ion with three groups has a planar or pyramidal structure. A pyramidal structure is always found where, in addition to the three groups, a lone electron pair is present. This occupies, as it were, the position of the fourth substituent in a tetrahedral arrangement. This rule is also valid for ions.

The structures of the complex ions in which, according to the formula, the central atom has the co-ordination number 3, have been determined by X-ray analysis and also confirmed in part by the characteristic infra-red frequencies. With X-ray analysis it has become apparent that the central atom in many complexes with the co-ordination number 3, particularly in halo-complexes, does not possess this co-ordination number in the lattice, but is co-ordinated to a greater extent. As far as such compounds dissolve in water, it must for the present remain undecided whether simple complexes are in fact present in aqueous solution, and what structures these have. Where the structure investigations of crystalline salts containing the appropriate complex ions have not been carried out, the question whether a complex with the co-ordination number 3 occurs must frequently be left open, as, for example, in lithium cupric chloride (p. 98), where the complex $CuCl_3'$ possibly occurs, or in $Cu^I(CN)_3''$ which, as already mentioned, is less stable than $Cu^I(CN)_4'''$, where the co-ordination number 4 is assured

⁶⁶ The angle for the trihalides of group V elements is in the neighbourhood of 100°: A. H. GREGG, G. C. HAMPSON, G. I. JENKINS, P. L. F. JONES and L. E. SUTTON, *Trans. Faraday Soc.*, 1937, **33**, 852.

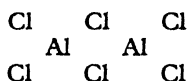
⁶⁷ L. C. PAULING and L. O. BROCKWAY, *J. Am. Chem. Soc.*, 1935, **57**, 2684. New electron-diffraction calculation (radial distribution method; according to the visual method, a rather larger distance and a somewhat smaller angle).

⁶⁸ O. HASSEL and A. SANDBO, *Z. physik. Chem.*, 1938, **B 41**, 75 (electron diffraction).

⁶⁹ A. BYSTRÖM and A. F. WESTGREN, *Arkiv Kemi Min. Geol.*, 1943, **17 B**, No. 2.

⁷⁰ E. LEE and C. K. WU, *Trans. Faraday Soc.*, 1939, **35**, 1366; 1373 (infra-red spectrum).

tain SiO_3'' and PO_3' ions respectively. In reality, linking up of SiO_4 and PO_4 tetrahedra occurs here. These compounds are thus to be included among the *isopoly-acids*, and will be respectively discussed along with these and the silicates. In them the central atom has the co-ordination number 4. In general, compounds and ions, which, according to their stoichiometric composition, contain central atoms with the co-ordination number 3, strive very frequently to attain a higher co-ordination number, much more frequently than those containing the co-ordination number 4. This becomes apparent in compounds of the first order on the formation of lattices which, on the whole, are really tightly packed, or of double molecules. The aluminium halides present a good example of this. From AlCl_3 the double molecule Al_2Cl_6 is formed, in which each aluminium atom has the co-ordination number 4:



AlBr_3 and AlI_3 similarly form double molecules (p. 168), but AlF_3 , by contrast, forms a stable spatial lattice in which AlF_6''' complexes are linked among themselves, the aluminium thus having the co-ordination number 6. This will be dealt with in detail later with the volatility of inorganic compounds (Chapter III, p. 168, and Chapter VII, 3, (iv)).

Oxygen-containing anions, written formally as XO_3 , can owe their composition not only to a chainlike linking of XO_4 tetrahedra as in the silicates and phosphates, but also to an interlinking of XO_6 octahedra. In these, as with compounds of the first order, the central atom can thus have the co-ordination number 6 as well as the co-ordination number 4. Only X-ray analysis can decide between the structure types. As an example of the co-ordination number 6, *perovskite* CaTiO_3 may be quoted as a type possessing a lattice structure which occurs especially frequently. This occurs in the compounds NaNbO_3 , NaTaO_3 , LaGaO_3 , LaAlO_3 , LaFeO_3 and KIO_3 ⁷⁴, among others, as well as in complex fluorides such as KNiF_3 ⁷⁵.

Perovskite itself and various compounds of the same type contain somewhat deformed XO_6 octahedra in the lattice, and consequently possess only a pseudo-cubic, monoclinic symmetry⁷⁶. On the other hand, the idealized perovskite type, which is realized with other compounds of the general formula MXO_3 , e.g., barium titanate BaTiO_3 and barium zirconate BaZrO_3 , possesses a strictly cubic symmetry.

The elementary unit of this idealized perovskite type is shown in Fig. 15. In it, to be sure, only the co-ordination number 12 for the central cal-

⁷⁴ Otherwise than in NaIO_3 , in which the IO_3' ion is an isolated pyramidal ion (see Chapter VIII, 3).

⁷⁵ A. E. VAN ARKEL, *Physica*, 1925, [i], 5, 162 (KMgF_6). Cf. V. M. GOLDSCHMIDT, *Geochemische Verteilungsgesetze VIII, Skrifter Norske Videnskaps-Akad. Oslo, Mat.-nat. Klasse*, 1926. No. 8.

⁷⁶ S. VON NÁRAY-SZABÓ, *Naturwissenschaften*, 1943, 31, 202.

cium atom can be seen. However, if the lattice is thought of as continued in all directions, it is at once apparent that the titanium atoms situated at the corners of the elementary cube are octahedrally surrounded by six oxygen

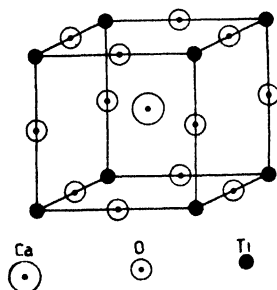
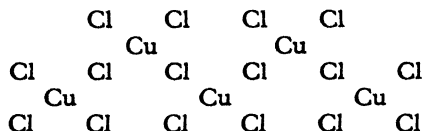


Fig. 15. Lattice of the perovskite crystal type

atoms, with the TiO_6 octahedra connected to one another by corners. Each oxygen atom is thus attached to two titanium atoms, so that with the infinite linking of octahedra half as much oxygen is present relative to titanium as in a single octahedron, in accordance with the formula CaTiO_3 . In addition, an infinite linking of XO_6 octahedra in a compound of the first order without the ion situated at the centre of the elementary unit, also occurs in rhenium trioxide⁷⁷.

The titanates, niobates, etc., known only in the crystalline state, used not to be reckoned to the complex compounds any more than were the metasilicates; but, as the forementioned examples of the iodates and of potassium nickel fluoride show, this is by no means justifiable. A difference exists only to the extent that, like the typical saltlike complexes which can be brought into solution, the simple molecular complex with the co-ordination number 3 is apparently formed in solution. A few further examples of such complexes will be cited here.

The salt CsCuCl_3 (pp. 98–99) does not contain an isolated complex ion in the lattice, but planar CuCl_4 complexes connected by chlorine atoms to form chains:



The caesium ions are spirally arranged about these chains which traverse the crystal⁷⁸. The salts NH_4CdCl_3 , $\text{Pb}(\text{CdCl}_3)_2$, NH_4HgCl_3 and CsHgCl_3 also belong here. In the lattice, the central atom has the co-ordination number 6 and is octahedrally surrounded by chlorine atoms, so that the complexes $[\text{CdCl}_6]$ and $[\text{HgCl}_6]$ occur. They are, however, not isolated, but linked together in various ways. In the complex cadmium salts, the octahedra form

⁷⁷ K. MEISEL, *Z. anorg. Chem.*, 1932, **207**, 12. CrO_3 is similarly constructed.

⁷⁸ A. F. WELLS, *J. Chem. Soc.*, 1947, p. 1662.

in one direction non-isolated double chains⁷⁹, these being held together by ammonium ions situated between them. In $\text{NH}_4[\text{HgCl}_3]$ they form layers⁸⁰, and in $\text{Cs}[\text{HgCl}_3]$ they are spatially interlinked in a perovskite structure⁸¹. The octahedra are not regular as in CaTiO_3 , but deformed in such a way that two chlorine atoms are situated nearer to the mercury than the others. To a certain extent, therefore, HgCl_2 molecules appear to be represented in the lattice, a transition from a complex to a double salt occurring. Another related example of the perovskite structure for a complex salt is the sparingly soluble caesium argentous auric chloride, $\text{Cs}_2\text{AgAuCl}_6 = \text{CsAgCl}_3 \cdot \text{CsAuCl}_3$, which has found application in the microchemical estimation of caesium. Very similar in construction is caesium aurichloride CsAuCl_3 with a deformed perovskite structure⁸². This also does not correspond to CsCuCl_3 , but is to be written $\text{Cs}_2\text{Au}^{\text{I}}\text{Au}^{\text{III}}\text{Cl}_6$. Planar AuCl_4^- groups with trivalent gold and linear AuCl_2^- groups with monovalent gold — to be compared with the linear structure of the analogous complexes of silver (see later) — can be recognized in its lattice.

(iv) Co-ordination Number 2

Little is known concerning the spatial structure of complexes with the co-ordination number 2 as they occur, by way of example, in the ion $\text{Ag}(\text{NH}_3)_2^+$ ⁸³, in the dicyano-complexes $\text{Ag}(\text{CN})_2^-$ and $\text{Au}(\text{CN})_2^-$, in t' thiosulphato-complexes $\text{Ag}(\text{S}_2\text{O}_3)_2^{2-}$, $\text{Cu}(\text{S}_2\text{O}_3)_2^{2-}$ and $\text{Au}(\text{S}_2\text{O}_3)_2^{2-}$ in nitrites and chlorites and in the iodonium compounds. The ions $\text{Ag}(\text{NH}_3)_2^+$ and $\text{Ag}(\text{CN})_2^-$ possess a linear structure in the lattice⁸⁵. From a structure investigation of ammonium chlorite NH_4ClO_2 , a bent structure for the chlorite ion ClO_2^- has been determined with a $\text{Cl}-\text{O}$ distance of 1.6 Å. More thorough structure investigations exist for the nitrites. In sodium nitrite⁸⁶, potassium nitrite⁸⁷ and silver nitrite⁸⁸, the nitrite group is bent at an angle of 132° with an $\text{N}-\text{O}$ distance of 1.14 Å, and likewise in nitro-complexes, e.g., in silver diammino-tetranitro-cobaltiate $\text{Ag}[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]$ ⁸⁹. Whether the angles and distances in all these instances are exactly the same

⁷⁹ H. BRASSEUR and L. C. PAULING, *J. Am. Chem. Soc.*, 1938, **60**, 2886.

⁸⁰ E. J. HARMSSEN, *Z. Krist.*, 1938, **100**, 208.

⁸¹ Similarly for $\text{Cs}[\text{CdCl}_3]$, $\text{Cs}[\text{CdBr}_3]$ and $\text{Cs}[\text{HgBr}_3]$, which all possess a perovskite structure: A. FERRARI and A. BARONI, *Atti R. Accad. Lincei*, 1927, [vi], **6**, 418; G. NATTA and L. PASSERINI, *Gazz. chim. ital.*, 1928, **58**, 472.

⁸² A. F. WELLS, *J. Chem. Soc.*, 1947, p. 1669.

⁸³ That the complex contains only two molecules of ammonia follows from the fact that on electrolysis two moles of ammonia are liberated at the cathode for one g-atom of silver: C. DUVAL, *Compt. rend.*, 1935, **200**, 2175. Cf. also H. EULER, *Ber.*, 1903, **36**, 1854. Proof by potentiometric titration: R. NÄSÄNEN, *Acta Chem. Scand.*, 1947, **1**, 763.

⁸⁴ X-ray analysis of $[\text{Ag}(\text{NH}_3)_2]_2\text{SO}_4$: R. B. COREY and R. W. G. WYCKOFF, *Z. Krist.*, 1934, **87**, 264.

⁸⁵ J. L. HOARD, *Z. Krist.*, 1933, **84**, 231.

⁸⁶ G. E. ZIEGLER, *Phys. Rev.*, 1931, [ii], **38**, 1040.

⁸⁷ G. E. ZIEGLER, *Z. Krist.*, 1936, **94**, 491.

⁸⁸ J. A. A. KETELAAR, *Z. Krist.*, 1936, **95**, 383.

⁸⁹ A. F. WELLS, *Z. Krist.*, 1936, **95**, 74.

as in the alkali salts containing the nitrite ion may well be doubted, for with the same structure of the atomic group $\text{O} \begin{array}{c} \diagdown \\ \text{N} \\ \diagup \\ \text{O} \end{array}$ a characteristic

difference appears between the alkali nitrites and silver nitrite. In the silver nitrite lattice, the silver ion is situated nearer to the nitrogen of the nitrite ion than to its oxygen atoms, so that the symbolism $\text{Ag}-\text{NO}_2$ has a certain justification. This constitution of solid silver nitrite makes the difference in its behaviour from that of the alkali nitrites in the reaction with alkyl iodides understandable. In this it reacts — though not exclusively, nevertheless preponderantly — to form nitro-compounds $\text{R}-\text{NO}_2$, while the alkali nitrites, in which the nitrite ion comes into reaction with the halide, supplies the alkyl nitrite $\text{R}-\text{ONO}$.

In the case of volatile first-order compounds with the co-ordination number 2, it can easily be decided by reason of the dipole moment, or by the diffraction of X-rays or electrons, whether the structure is linear or bent. The following possess no dipole moment and therefore have linear structures: CO_2 , CS_2 , HgCl_2 , HgBr_2 , HgI_2 . The mercury dialkyls and diaryls, as well as the ion $\text{Tl}(\text{CH}_3)_2^+$ in $[\text{Tl}(\text{CH}_3)_2]\text{Cl}^{90}$ also belong here. Carbon oxy-sulphide is likewise linear, but on account of the difference in the substituents possesses a dipole moment (cf. p. 345). According to electron-diffraction patterns, TeCl_2 , TeBr_2 and TeI_2 are linear or nearly linear with an angle of at least 150° and atomic distances 2.36, 2.49 and 2.70 \AA^{91} .

H_2O , H_2S and SO_2 possess bent structures and dipole moments of 1.8, 0.9 and 1.7 units respectively: likewise NO_2 , which has a very small moment. Compounds such as F_2O and ClO_2 must also possess dipole moments, for bent structures have been determined for them by electron diffraction: about 100° for $\text{F} \begin{array}{c} \diagdown \\ \text{O} \\ \diagup \\ \text{F} \end{array}$ with an $\text{F}-\text{O}$ distance of 1.41 \AA^{92} ; about 115° for $\text{Cl} \begin{array}{c} \diagdown \\ \text{O} \\ \diagup \\ \text{Cl} \end{array}$ with a $\text{Cl}-\text{O}$ distance of 1.68 \AA^{92} ; about 140° for $\text{O} \begin{array}{c} \diagdown \\ \text{Cl} \\ \diagup \\ \text{O} \end{array}$.

(v) Co-ordination Number 5

Complexes with the co-ordination number 5 are not known with certainty. In the cases in which, according to the empirical formulae, complexes can be constructed with the co-ordination number 5, it has almost always been found that other constructions have had to be assigned to the compounds. Thus with the various pentahydrates such as $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, one molecule of water is allotted to the anion, while the cation is present as a tetraquo-complex. In addition, a corresponding subdivision of the water molecules

⁹⁰ H. M. POWELL and D. M. CROWFOOT, *Z. Krist.*, 1934, **87**, 370.

⁹¹ W. GREYER, *Ann. Physik*, 1936, [v], **26**, 1. TeBr_2 , angle 98° : M. T. ROGERS and R. A. SPURR, *J. Am. Chem. Soc.*, 1947, **69**, 2102.

⁹² H. BOERSCH, *Sitzungsber. Akad. Wiss. Wien, Math.-nat. Kl.*, IIB, 1935, **144**, 1; *Monatsh.*, 1935, **65**, 311; L. E. SUTTON and L. O. BROCKWAY, *J. Am. Chem. Soc.*, 1935, **57**, 473.

is to be undertaken in the numerous heptahydrates such as $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, in which occurs not a cation with the co-ordination number 7, but a hexaquo-cation and a sulphate ion likewise hydrated by one molecule of water. An assignation of water molecules to the anion cannot by any means always be undertaken with certainty, and the arrangement of the water molecules remains undecided (for further, see p. 136). Further examples of empirical formulae with the apparent co-ordination number 5 having to be solved quite otherwise are the previously mentioned compounds Cs_3CoCl_5 (pp. 119–120) and $(\text{NH}_4)_3\text{ZnCl}_5$, which, according to their crystal structure, are to be formulated $\text{Cs}_2\text{CoCl}_4 \cdot \text{CsCl}$ and $(\text{NH}_4)_2\text{ZnCl}_4 \cdot \text{NH}_4\text{Cl}$. In the insoluble compound Tl_2AlF_5 , known only in the crystalline state, the co-ordination number 5 is simulated in the lattice by a chain-formation of AlF_6 octahedra (pp. 123, 124).

At the same time, it is not excluded that complexes with the co-ordination number 5 do occur on occasions⁹³, for, with the elements of groups V and VI, compounds of the first order exist in which the co-ordination number of the central atom is 5, that is to say, the pentahalides. As far as their structures in the gaseous state have been investigated by electron diffraction, which is the case for FF_5 , PCl_5 , PF_3Cl_2 , SbCl_5 and MoCl_5 ⁹⁴, each forms a trigonal bipyramid (Fig. 16). The same is true of iron

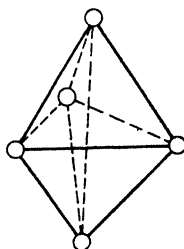


Fig. 16. Trigonal bipyramid

pentacarbonyl (Chapter VII, 7, (v)) and at least very probably so for iodine pentafluoride IF_5 ⁹⁵. In many cases the bipyramid possesses the symmetry D_{3h} of the trigonal holohedral class, which follows from the absence of a dipole moment⁹⁶. For PCl_5 in carbon disulphide solution it is quite small (0.8 D⁹⁷), and probably to be ascribed to a slight deformation of the molecule in solution. This may also be the case for TaCl_5 , whose moment in carbon disulphide is nevertheless 1.2 D⁹⁸. In none of the cases thus far investigated are the five halogen atoms arranged about the central atom in a planar

⁹³ The co-ordination number 5 has on very rare occasions been determined for a crystal lattice. An example is andalusite Al_2SiO_5 (Chapter VIII, 4, (iii)), in which the aluminium atom has the co-ordination number 5.

⁹⁴ R. V. G. EWENS and M. W. LISTER, *Trans. Faraday Soc.*, 1938, **34**, 1358.

⁹⁵ H. BRAUNE and P. PINNOW, *Z. physik. Chem.*, 1937, **B 35**, 239.

⁹⁶ PF_5 : R. LINKE and W. ROHRMANN, *Z. physik. Chem.*, 1937, **B 35**, 256.

⁹⁷ P. TRUNEL, *Compt. rend.*, 1936, **202**, 37.

⁹⁸ H. MOUREU, *Compt. rend.*, 1936, **202**, 314.

pentagon. Data characterizing the structure, have been specifically determined for the following:

molecule		distance (Å)		distance (Å)	distance (Å)
PCl_5^{99}	P—Cl basal	2.04	P—Cl apical	2.19	Cl—Cl 3.08
SbCl_5^{99}	Sb—Cl	2.31	Sb—Cl	2.43	
PF_5^{100}	P—F	1.57	P—F	1.57	
$\text{PF}_3\text{Cl}_2^{100}$	P—F	1.59	P—Cl	2.05	

In the crystalline state, the spatial structure of the pentahalides may of course be quite different. With the relatively involatile compounds PCl_5 and PBr_5 , at any rate, an ionic lattice is present. For PCl_5 , a lattice built up of $[\text{PCl}_4]^+$ and $[\text{PCl}_6]^-$ ions¹⁰¹ follows from powder exposures according to the DEBYE-SCHERRER method in agreement with the RAMAN spectrum, whereas for PBr_5 the lattice is built up of $[\text{PBr}_4]^+$ and Br^- ions¹⁰². On the other hand, PF_5 may form a molecular lattice with undistorted or only slightly distorted molecules.

(vi) Co-ordination Number 7

The only known first-order compound with the co-ordination number 7, iodine heptafluoride IF_7 , although it is highly volatile (m.p. under pressure 5.5° , b.p. 4.5°), has not yet been investigated with respect to its spatial structure. The elements niobium, tantalum and zirconium in the fluoniobates NbF_7'' , fluotantalates TaF_7'' and fluozirconates ZrF_7''' form complexes with the co-ordination number 7. This has been demonstrated with certainty by the X-ray analysis of various salts, as in the cases of K_2NbF_7 and K_2TaF_7 ¹⁰³. The anion forms a trigonal prism with six fluorine atoms at the corners and one fluorine atom vertically above the base of the prism (Fig. 17). The ZrF_7''' ion¹⁰⁴ is constructed somewhat differently from NbF_7'' and TaF_7'' . The Nb—F distances in the NbF_7'' ion are 1.96 Å for six fluorine atoms

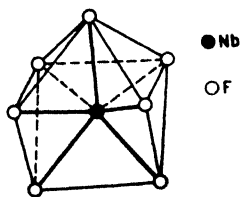


Fig. 17. Configuration of the NbF_7'' ion. The distances of the individual fluorine atoms from the niobium atom are not very different: Nb—F 1.98 (2), 1.96 (2), 1.94, 1.95, 2.01 Å.

⁹⁹ M. ROUAULT, *Ann. phys.*, 1940, [xi], 14, 78 (electron diffraction). Improved results relative to *Compt. rend.*, 1938, 207, 620.

¹⁰⁰ L. O. BROCKWAY and J. Y. BEACH, *J. Am. Chem. Soc.*, 1938, 60, 1836. Also PF_5 : H. BRAUNE and P. PINNOW, *Z. physik. Chem.*, 1937, B 35, 239.

¹⁰¹ A. M. DE FICQUELMONT, G. WETROFF and H. MOUREU, *Compt. rend.*, 1940, 211, 566.

¹⁰² H. M. POWELL and D. CLARK, *Nature*, 1940, 145, 971.

¹⁰³ J. L. HOARD, *J. Am. Chem. Soc.*, 1939, 61, 1252.

¹⁰⁴ G. C. HAMPSON and L. C. PAULING, *J. Am. Chem. Soc.*, 1938, 60, 2702.

and 2.01 Å for the seventh atom, with F—F distances 2.11 and 2.98 Å respectively.

These complex fluorides are thus *not*, as had formerly been assumed on the basis of an inadequate structure determination for $(\text{NH}_4)_3\text{ZrF}_7$, to be formulated as a kind of double salt with the co-ordination number 6, e.g., $(\text{NH}_4)_2\text{ZrF}_6 \cdot \text{NH}_4\text{F}$, analogously to $\text{Cs}_2\text{CoCl}_4 \cdot \text{CsCl}$.

Whether the co-ordination number 7 is to be assumed in the complex for other compounds with a formally analogous constitution, or whether the formulae are to be interpreted with a complex, which in the lattice corresponds to the co-ordination number 6, is a question which must be left open. This is so, for example, with the compound $3\text{NH}_4\text{F} \cdot \text{SiF}_4$, which is known in addition to the usual ammonium fluosilicate $(\text{NH}_4)_2\text{SiF}_6$ and formed when a solution of fluosilicic acid is decomposed with ammonium fluoride and neutralized with ammonia.

(vii) Co-ordination Number 8

The symmetrical distribution of eight groups about a central atom is their arrangement at the corners of a cube. In the complexes thus far investigated, however, this arrangement is not realized. In the salt $\text{K}_4[\text{Mo}(\text{CN})_8] \cdot 2\text{H}_2\text{O}$, which is isomorphous with the salt $\text{K}_4[\text{W}(\text{CN})_8] \cdot 2\text{H}_2\text{O}$, the cyano groups in the $\text{Mo}(\text{CN})_8^{4-}$ complex form a dodecahedron with triangular sides and eight corners¹⁰⁵ (Fig. 18). With $\text{K}_4\text{U}(\text{C}_2\text{O}_4)_4 \cdot 5\text{H}_2\text{O}$, the oxalato radicals in the anion $\text{U}(\text{C}_2\text{O}_4)_4^{4-}$ are not able to occupy the corners of a cube, since it occurs as optical enantiomorphs. In point of fact, a pair of

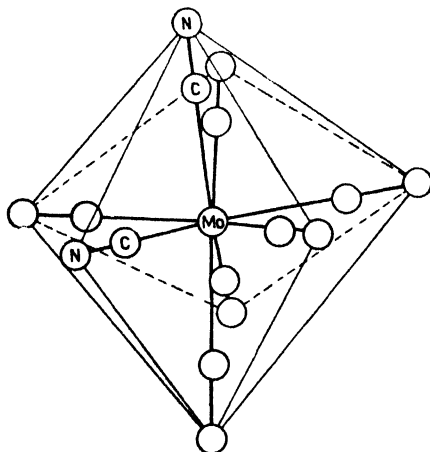


Fig. 18. Structure of the $\text{Mo}(\text{CN})_8^{4-}$ ion

¹⁰⁵ J. L. HOARD and H. H. NORDSIECK, *J. Am. Chem. Soc.*, 1939, **61**, 2853. Concerning compounds with the co-ordination number 8 and a compilation of the geometrically possible configurations, see L. E. MARCHI, W. C. FERNELIUS and J. P. McREYNOLDS, *J. Am. Chem. Soc.*, 1943, **65**, 330; (corrected) 1944, **66**, 1984.

stable *d* and *l* modifications are known, together with a pair of easily racemizable *d* and *l* modifications¹⁰⁶.

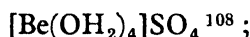
(viii) Co-ordination Number 9

The co-ordination number 9 has been demonstrated by X-ray analysis for neodymium in neodymium bromate, which is accordingly enneaquoneodymium bromate $[\text{Nd}(\text{OH}_2)_9](\text{BrO}_3)_3$. Here the $9\text{H}_2\text{O}$ are thus not to be divided as usual between cation and anion into $6\text{H}_2\text{O} + 3\text{H}_2\text{O}$ ¹⁰⁷, as is the case, for example, in $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$.

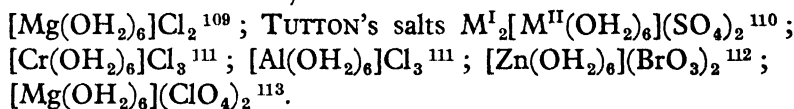
4. Water of Crystallization

The so-called water of crystallization is in many cases water bound to the cation in an aquo-complex, in the manner formulated by WERNER. It has frequently been possible to confirm this directly by X-ray analysis. Examples for this are:

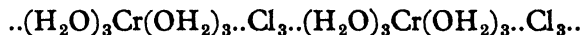
(co-ordination number 4)



(co-ordination number 6)



However, the complex formula with independent chloride ions is incomplete in $[\text{Cr}(\text{OH}_2)_6]\text{Cl}_3$ and $[\text{Al}(\text{OH}_2)_6]\text{Cl}_3$, inasmuch as the chloride ions in the lattice effect a bond to the water molecules, which follows from the spatial proximity of the chlorine and oxygen atoms (3.1 Å). Each Cl' is connected with three H_2O from different octahedra and each H_2O with two Cl' in such a way that chains



thereby arise, which traverse the crystal. On the other hand, $[\text{Mg}(\text{OH}_2)_6]\text{Cl}_2$ forms isolated structural groups in the lattice. (See also Chapter VIII, 7, (ii) and Chapter XI, 3, (iii)).

Analogously constructed to the strictly heteropolar magnesium perchlorate hexahydrate is lithium perchlorate trihydrate $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$ ¹¹⁴ which, in

¹⁰⁶ L. E. MARCHI, W. C. FERNELIUS and J. P. McREYNOLDS, *J. Am. Chem. Soc.*, 1943, **65**, 330.

¹⁰⁷ L. HELMHOLZ, *J. Am. Chem. Soc.*, 1939, **61**, 1544.

¹⁰⁸ C. A. BEEVERS and H. LIPSON, *Z. Krist.*, 1932, **82**, 297.

¹⁰⁹ K. R. ANDRESS and J. GUNDERMANN, *Z. Krist.*, 1934, **87**, 345. Likewise $[\text{Mg}(\text{OH}_2)_6][\text{H}_2\text{PO}_4]_2$; A. FERRARI and C. COLLA, *Gazz. chim. ital.*, 1937, **67**, 297.

¹¹⁰ W. HOFMANN, *Z. Krist.*, 1931, **78**, 279; 1932, **82**, 323.

¹¹¹ K. R. ANDRESS and C. CARPENTER, *Z. Krist.*, 1934, **87**, 446.

¹¹² S. H. YÜ and C. A. BEEVERS, *Z. Krist.*, 1937, **95**, 426.

¹¹³ C. D. WEST, *Z. Krist.*, 1935, **91**, 480.

¹¹⁴ C. D. WEST, *Z. Krist.*, 1934, **88**, 198.

order to bring out the lattice analogy with magnesium perchlorate, is better written $\text{Li}_2(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O} = [\text{LiLi}(\text{OH}_2)_6](\text{ClO}_4)_2$. The positions in the lattice taken up by the unhydrated lithium ions are unoccupied in the magnesium perchlorate lattice. The isomorphous lithium fluoborate trihydrate $\text{LiBF}_4 \cdot 3\text{H}_2\text{O}$ has the similar structure $[\text{LiLi}(\text{OH}_2)_6][\text{BF}_4]_2$ ¹¹³.

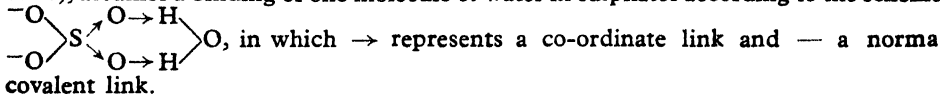
If the composition of a salt containing water of crystallization does not correspond to an aquo-complex with the co-ordination number 4 or 6, the number of water molecules in excess of 4 or 6 have usually to be accounted for as exo-aquo molecules^{114a} elsewhere, and are to be placed in the anion as water of hydration¹¹⁵ (cf. also the isomeric chromic chloride hexahydrates p. 100 ff). This has been identified by X-ray analysis only in isolated cases, as for cupric sulphate $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ¹¹⁶ and nickel sulphate $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ ¹¹⁷. In cupric sulphate the four water molecules of the aquo-cation do not form a tetrahedron, but are arranged in a planar fashion; they form with two more distant oxygen atoms belonging to two SO_4'' ions an irregular octahedron. In $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$, the aquo-cation is also a distorted octahedron: in $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, on the contrary, the structure of the $[\text{Ni}(\text{OH}_2)_6]^{2+}$ ion is strictly octahedral.

In lithium sulphate monohydrate $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$, however, the water does not belong to the sulphate ion¹¹⁸, but the lattice structure is such that two kinds of lithium ions are present in the lattice. The water belongs to one kind where the lithium atom is tetrahedrally surrounded by four oxygen atoms, of which one is from the water molecule and the others from three SO_4'' ions. The other kind of lithium atom is surrounded by four oxygen atoms belonging to SO_4'' ions.

For the *alums* typified by $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, as has been demonstrated by X-ray analysis, the hydration of the aluminium ion is the same as in hydrated aluminium chloride, where a hexaquo-cation is present¹¹⁹. The other six water molecules surround the potassium ion octahedrally, though at such a large distance — from the potassium to the oxygen 2.94 Å — that a normal hexaquo-cation $\text{K}(\text{OH}_2)_6^+$ cannot be assumed. These six molecules of water are also, as is seen on dehydrating the alum, very loosely bound in the

^{114a} The term *Exo-aquomoleküle* was coined by WERNER for water molecules loosely bound in the anion.

¹¹⁵ N. V. SIDGWICK, on p. 195 of *The Electronic Theory of Valency*, (Oxford, 1927), assumes a binding of one molecule of water in sulphates according to the scheme



¹¹⁶ C. A. BEEVERS and H. LIPSON, *Proc. Roy. Soc.*, 1934, **A** 146, 570.

¹¹⁷ C. A. BEEVERS and C. M. SCHWARTZ, *Z. Krist.*, 1935, **91**, 157.

¹¹⁸ G. E. ZIEGLER, *Z. Krist.*, 1934, **89**, 456. The opposite indication given by H. J. EMELÉUS and J. S. ANDERSON in *Modern Aspects of Inorganic Chemistry*, p. 159, is not correct.

¹¹⁹ C. A. BEEVERS and H. LIPSON, *Nature*, 1934, **134**, 327; H. LIPSON and C. A. BEEVERS, *Proc. Roy. Soc.*, 1935, **A** 148, 664. Caesium alum and methylammonium alum crystallize with a somewhat different type of lattice, a third type being sodium alum: H. LIPSON, *Nature*, 1935, **135**, 912; *Proc. Roy. Soc.*, 1935, **A** 151, 347; *Phil. Mag.*, 1935, [vii], **19**, 887.

lattice. With these it is consequently possible to speak of water of crystallization in the real sense of the word. As one detailed examination of the atomic arrangement shows¹²⁰, the oxygen atoms of the two kinds of water molecules are at a distance of about 2.5 Å, that is, nearer than in ice (Chapter VII, 2, (ii)), so that with WERNER it is possible to speak of double molecules, H_4O_2 , which are held together by means of a hydrogen bond.

In many cases, it is only X-ray analysis which can provide any sort of information concerning the manner of binding of the so-called water of crystallization. Many of the earlier conjectures which rested on a formal application of the co-ordination theory have in consequence been demonstrated more recently to be untenable. A few further examples of this may be given. Cupric chloride dihydrate $CuCl_2 \cdot 2H_2O$ ¹²¹, known as a mineral as antofagastite, is neither diaquo cupric chloride $[Cu(OH_2)_2]Cl_2$ nor a salt with hydrated chloride ions $Cu(Cl \cdot HOH)_2$ somewhat analogous to the green chromic chloride hexahydrates, but $\begin{matrix} H_2O & Cl \\ & \diagdown \quad / \\ & Cu \\ & / \quad \diagdown \\ Cl & OH_2 \end{matrix}$, to be classed with the non-electrolytes of the type of *trans*-dichloro-diammine platinum $Cl_2Pt^{II}(NH_3)_2$ ¹²². In the planarly constructed complex, the Cu—Cl distance is 2.32 and that of Cu—O 1.97 Å. The distance between the copper and an oxygen atom of the water is nearly the same as in tenorite CuO, namely 1.95 Å. Exactly the same structure occurs again in the "complex salt" $K_2CuCl_4 \cdot 2H_2O$ ¹²³: the Cu and 2Cl (distance 2.30 Å) and 2O (distance 2.01 Å) lie in one plane forming a rhombus; vertically above and below the copper atom are two further chlorine atoms at a distance of 2.99 Å. The latter distance is so large, that a real chemical bond effected by an electron pair between each of these chlorine atoms and the central atom cannot be assumed, especially as the distance from the copper to the chlorine in the neighbouring layers of the "non-electrolyte molecule" $(H_2O)_2CuCl_2$ is practically the same. It is therefore not correct to formulate the complex salt $K_2CuCl_4 \cdot 2H_2O$ as a complex in which the copper has the co-ordination number 6, $K_2[CuCl_4 \cdot (OH_2)_2]$, although an octahedral configuration $[CuCl_4(OH_2)_2]$ is actually present. The octahedron, or, more correctly, tetragonal bipyramid, does not however contain four chlorine atoms in structurally equivalent positions at the common base of the pyramids, but has instead 2Cl and 2 H_2O ; and the apexes of the double pyramid are not occupied by water molecules, but by two chlorine atoms. Likewise the formulation $[K(OH_2)]_2[CuCl_4]$, which is suggested from the classical standpoint, is naturally false.

¹²⁰ K. SPANGENBERG, who also gives the interatomic distances, optical refractions and vapour pressures of various alums. See W. KLEMM and co-authors, *Inorganic Chemistry* III, p. 132 ff (*FIAT Review of German Science* 1939—1946, published 1948).

¹²¹ D. HARKER, *Z. Krist.*, 1936, **93**, 136.

¹²² *Trans*-dipyridino cupric chloride has exactly the same structure: E. G. COX, E. SHARRATT, W. WARDLAW and K. C. WEBSTER, *J. Chem. Soc.*, **1936**, p. 129.

¹²³ S. B. HENDRICKS and R. G. DICKINSON, *J. Am. Chem. Soc.*, 1927, **49**, 2149; L. CHROBAK, *Z. Krist.*, 1934, **88**, 35.

The double-salt formula still comes nearest to reality if it is written $2\text{KCl} \cdot [(\text{H}_2\text{O})_2\text{CuCl}_2]$, although it is of course unable to give a correct expression to the more distant relationship between the copper and the two chlorine atoms written with the potassium. Of what little help speculation on the basis of the classical co-ordination theory is, may be demonstrated further by reference to the complex salt $\text{K}_2\text{HgCl}_4 \cdot \text{H}_2\text{O}$. This is quite differently constructed with sixfold octahedral co-ordination of the mercury (p. 124). The water is situated here between potassium ions, one oxygen atom being co-ordinated with four of the latter ¹²⁴.

"Water of crystallization" is bound yet differently again in spaciouly constructed lattices, as in the hydrates of aluminium fluoride $\text{AlF}_3 \cdot \text{H}_2\text{O}$ and $2\text{AlF}_3 \cdot \text{H}_2\text{O}$ and in many silicates. This will be discussed elsewhere (see Chapter VIII, 7, (iii), and Chapter IX, Part I, 7).

The manner in which water molecules hold together the layers constructed of Ca^{++} ions and tetrahedral SO_4^{--} ions in gypsum is characteristic ¹²⁵. In Fig. 19 the very good cleavability of gypsum in the 010 direction is immediately apparent.

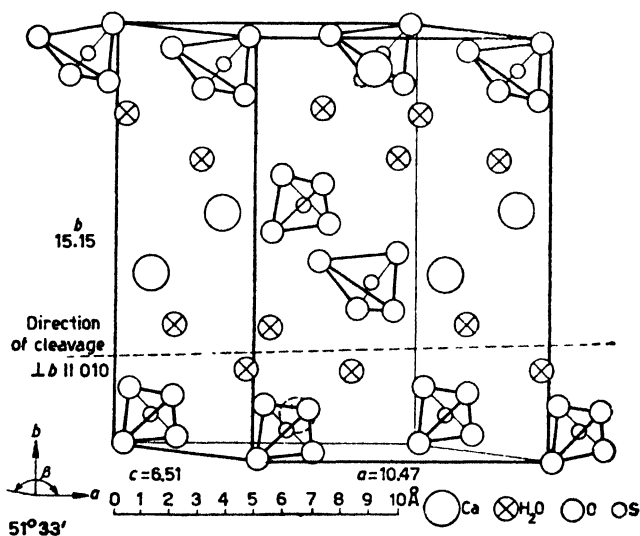


Fig. 19. Lattice of gypsum

Finally, how complicated the binding of water of crystallization in a lattice can be, is taught by the example of hydrated cadmium sulphate $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$, a rock upon which the classical co-ordination theory could grind itself to pieces without coming to a structural explanation. X-ray analysis ¹²⁶ has been able to explain the relationships completely, demonstrating

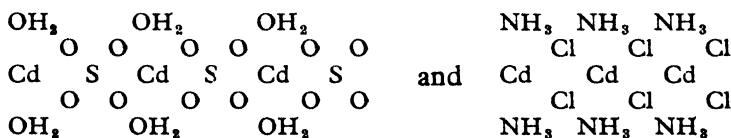
¹²⁴ C. H. MACGILLAVRY, J. H. DE WILDE and J. M. BIJVOET, *Z. Krist.*, 1938, **100**, 212.

¹²⁵ W. A. WOOSTER, *Z. Krist.*, 1936, **94**, 375.

¹²⁶ H. LIPSON, *Proc. Roy. Soc.*, 1936, **A 156**, 462; *Strukturber.* IV, 52; 182. In the columns of the table on p. 54, S II and O V are each to be read on one occasion instead of O IV and O VI.

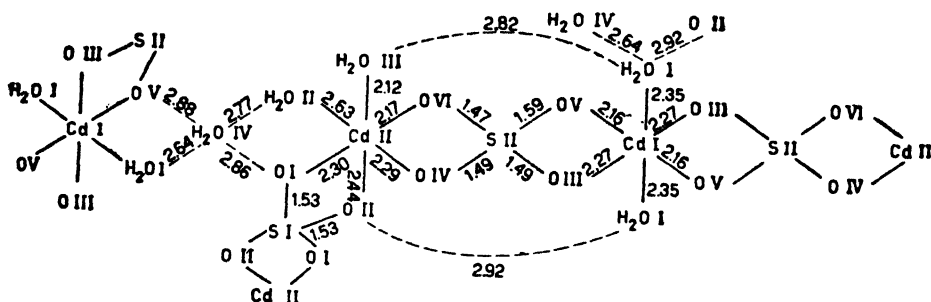
in a surprising way how far the principles of the co-ordination theory are individually realized in this by no means simply constructed lattice. Consequently this example is especially suited to constitute the close of this section on water of crystallization.

In the first place the formula is to be solved for $3\text{Cd}(\text{OH}_2)_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$, for of the $8\text{H}_2\text{O}$ only 6 are closely connected with the cadmium. The remaining two, which in the notation to be introduced subsequently will be denoted by $\text{H}_2\text{O IV}$, supply only a linking between two water molecules, as follows in detail from the diagram given later. If for the moment they are put on one side, $\text{Cd}(\text{OH}_2)_2\text{SO}_4$ remains as basic formula. It corresponds to the formula of the non-electrolyte type $\text{Cu}(\text{OH}_2)_2\text{Cl}_2$ or $\text{Cd}(\text{NH}_3)_2\text{Cl}_2$, and the structure in the lattice proves unequivocally that a sulphato-diaquo-cadmium group is present, in which the sulphato group occupies two co-ordination positions, and not rather a diaquo cadmium sulphate configuration. The linking up of the cadmium atoms is effected by means of sulphato groups as bridges, in which, however, otherwise than in the dichloro-complexes, *one* sulphato group suffices. From each, the oxygen atoms form the bridge in pairs, according to the principle: $\text{Cd} \begin{array}{c} \text{O} \quad \text{O} \\ \text{O} \quad \text{O} \end{array} \text{S} \begin{array}{c} \text{O} \quad \text{O} \\ \text{O} \quad \text{O} \end{array} \text{Cd} \begin{array}{c} \text{O} \quad \text{O} \\ \text{O} \quad \text{O} \end{array} \text{S} \begin{array}{c} \text{O} \quad \text{O} \\ \text{O} \quad \text{O} \end{array}$. The aquo molecules occupy the fifth and sixth co-ordination positions, so that the formulae



can be classed together. The tendency of cadmium to form compounds of the non-electrolyte type receives expression in both. But in the lattice the simple chain structure of the dichloro-diammine-complex is not found with the sulphato-diaquo-complex. The reason for this is the stereoisomerism of the sulphato-complex, which intrinsically would also be possible with the dichloro-complex, but does not make an appearance here. The two aquo molecules are able to occur both in the axial and edgewise positions. Both configurations are in fact realized in the lattice of cadmium sulphate, so that there are consequently two kinds of cadmium atoms. The first, Cd I, is surrounded by oxygen atoms from two aquo molecules in the *trans* configuration and oxygen atoms from two sulphato groups in an almost regular octahedron. The second, Cd II, with the *cis* configuration for the aquo molecules, exhibits an irregular octahedron as co-ordination polyhedron. There are also two kinds of sulphato groups, one, $\text{SO}_4 \text{ I}$, being a regular tetrahedron which links only Cd II atoms with one another (by means of O atoms I and II in the diagram), and the other a rather irregular tetrahedron which provides the bridge between Cd I and Cd II (by means of O atoms III and V to Cd I, and IV and VI to Cd II). The molecules of the genuine

water of crystallization in excess of the non-electrolyte formula effect further a special binding from one O of sulphato group I to Cd II, from one O of sulphato group II to Cd I, from one aquo molecule to Cd I, and from the aquo molecule furthest from the cadmium to Cd II. The accompanying diagram reproduces the linking of the atoms with the interatomic distances in Å.



A perspective diagram of the spatial lattice does not illustrate these points directly. The projection is drawn so that the atoms present in the axial configuration are always diametrically opposite. The rather close spatial proximity of H₂O I and H₂O III and of H₂O I and O II does not appear in the projection on account of the distortion. Distances along the edges of the octahedra and tetrahedra are not included, although in part they closely agree with the distances from the central atom. For example, H₂O II—H₂O III is 2.1 Å.

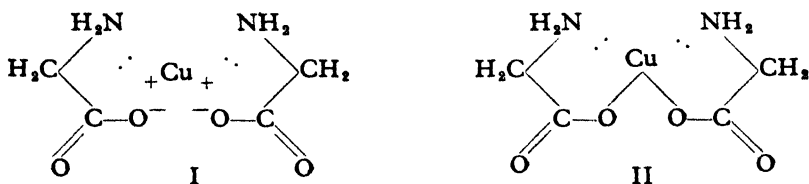
The stoichiometric ratios of 3Cd(OH₂)₂SO₄·2H₂O follow from the numbers of different bonds in the lattice. Each Cd I atom is firmly bound to two Cd II atoms by bridges effected by two SO₄ II groups, and further loosely bound to two other Cd II atoms via the aquo molecule H₂O I by means of two water molecules of crystallization H₂O IV. No links exist between two Cd I atoms. The Cd II atom, on the contrary, links itself on the one hand to a Cd II atom and on the other to a Cd I atom, each time with a sulphato group as bridge; and further is loosely attached to another Cd I atom by means of its aquo molecule H₂O II via H₂O IV and H₂O I. The same H₂O IV also provides links from O I to Cd II and from O V to Cd I.

Since firm bridge links radiate from one Cd I atom to two Cd II atoms, while from Cd II only one firm bridge leads to Cd I, and the second on the contrary to another Cd II, of the three bridges which radiate from three cadmium atoms, two are of the type Cd I—Cd II with SO₄ II as the binding medium, and one of the type Cd II—Cd II with SO₄ I as the binding medium. But since the number of sulphato bridges radiating from a Cd I atom is the same as the number of links through the water molecules of crystallization H₂O IV, the latter provide two-thirds of all the links between the cadmium atoms. In consequence, for every three cadmium atoms there are two water molecules of crystallization, as required by the formula 3Cd(OH₂)₂SO₄·2H₂O or the empirical formula 3CdSO₄·8H₂O.

5. Inner-complex Compounds

A special kind of complex compound, the *inner-complex compound*, occurs when two co-ordination positions on one central atom are filled by a single group, which in the two positions takes part in different kinds of links to the central atom. For one of the bonds, one atom of the group contributes a lone electron pair as the bonding pair of electrons. For the other bond, one of the electrons originates from another atom of the group and the second from the central atom. If the second of these two types of bonds is decidedly polar, as in the linking of an acido group to a metal atom in such a way that the latter "replaces" the acidic hydrogen atom, one speaks of an *inner-complex salt*. Of wider application is the term *inner-complex compound*, since, as will be demonstrated later, the saltlike polar bond can be so strong, that an ionic dissociation, such as is complete between an acid radical and a metal which is basic as hydroxide, is no longer effected by water, any more than it is, for example, in stable oxalato-complexes of the $\text{Cr}(\text{C}_2\text{O}_4)_3'''$ type. In the structural systematization of complex compounds, the inner-complex compounds belong to the group of *chelate compounds*¹²⁷, in which two or more co-ordination positions are occupied by a single group extending two or more "arms", as in the simplest case of complexes containing ethylenediamine. In the one case, as in the other, the atoms appended to the group form a ring with the central atom, the number of members being especially frequently five or six, sometimes seven, more rarely four or eight. In the older terminology, such rings were designated as subsidiary-valence rings (p. 86); and they are indeed purely subsidiary-valence rings in the usual chelate compounds, whereas in the inner-complex compounds, in which one bond can be spoken of at least formally as ionic, they are of mixed character.

The classical example of an inner-complex salt is the deep-blue *bis-glycino copper*¹²⁸. In this the nitrogen of the amino group is complexly bound to the copper by its lone electron pair, like the ammonia in the tetrammine-cupric ion. The carbonyl group of the aminoacetic acid behaves in a salt-forming manner, in which its hydrogen is replaced by copper. Since two glycine molecules are bound in the same way, formula I results, as follows:



This is not quite satisfying, inasmuch as the bond between the copper and

¹²⁷ From $\chi\eta\lambda\eta$, a claw (crab's claw).

¹²⁸ H. LEY, *Z. Elektrochem.*, 1904, **10**, 954; G. BRUNI, *ibid.*, 1905, **11**, 93; G. BRUNI and C. FORNARA, *Atti R. Accad. Lincei*, 1904, [v], **13**, 26. Cf. also H. LEY and H. WINKLER, *Ber.*, 1909, **42**, 3894; 1912, **45**, 372.

the carboxylate ion is not a decidedly heteropolar bond but, on account of the relatively small electron affinity of the carboxylate ion and the deformation of the Cu^{2+} ion, represents a transition to a homopolar bond. In point of fact, it can in principle be dissociated by water, as it is in aqueous solutions of cupric acetate, in which the cupric ion becomes hydrated, whereas the water is unable to loosen the firmer complex binding of the amino group. But for the unhydrated compound, a valence-line representing a homopolar bond in the formula between the Cu and O would likewise have a certain justification, so that formula II also appears to be quite reliable¹²⁹. Whether the ionization of the "semi-ionic" Cu—O bond really succeeds to a considerable degree in aqueous solution must for the moment remain an open question on account of the lack of experimental evidence. The not inconsiderable solubility of *bis*-glycine copper in water, by which it is distinguished from many other inner-complex salts, is presumably ascribable to such an ionization¹³⁰. Many inner-complex salts have in fact an exceptionally low solubility in water. With these the water is not in any case able to ionize the polar bond between the cationic central atom and the anionic acido group. Very remarkable differences in the solubility can occur, however. But whether these depend upon ionization of the saltlike bond of the inner complex by the water, or upon hydration of the central atom by direct addition of water with conservation of the complex in the soluble compounds, is for the time being an open question. This will be dealt with again later for the instances of the complexes of diacetyldioxime with the metals of the iron group and the acetylacetonates.

On account of their low solubility and in part definitely specific differences in solubility, various inner-complex salts have obtained an importance in analytical chemistry. Since the substituents which form the complex are organic compounds and the kind of bonding to the central atom is dependent on their constitution, it appears to be expedient to treat organic reagents in inorganic analytical chemistry along with their complexes in organic chemistry¹³¹. Hence only a few examples will find place here.

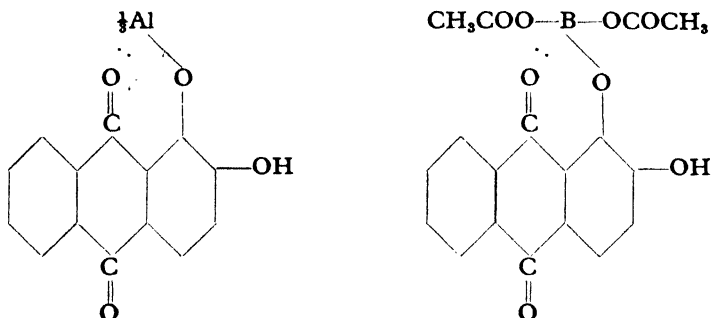
The *alizarin lakes* and related compounds, of which the alizarin lake of aluminium serves as a well-known sensitive test for this element, contain

¹²⁹ There are also compounds which according to their structure could be inner-complex salts, but in reality do not have the groups bound to the central atom in two co-ordination positions in their lattices. In these the ionic bond preferably provides a link with another atom or with a neighbouring central atom, so that instead of a ringlike structure an open ionic structure occurs without chelate bonding. Typical representations of this type of compound are the betaïnes, e.g., $(\text{CH}_3)_3\text{N}^+-\text{CH}_2-\text{COO}^-$, but such compounds also occur among inorganic complexes: P. PFEIFFER, *Z. anorg. Chem.*, 1936, **230**, 97. Cf. also F. HEIN, *J. prakt. Chem.*, 1931, [ii], **132**, 59.

¹³⁰ The fact that the correspondingly constructed *bis*-glycine zinc is completely hydrated by water in the course of time — and also partly hydrolyzed — that is, the complex bond as well as the saltlike bond is ruptured, also speaks for at least a partial ionization of the Cu—O bond.

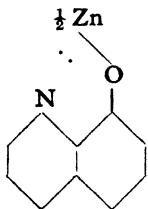
¹³¹ P. PFEIFFER, *Organische Molekülverbindungen (Chemie in Einzeldarstellungen, Vol. XI, Enke, Stuttgart, 2nd Ed., 1927)*.

the metal bound in a saltlike fashion to the phenolic hydroxyl group in the α position, and complexly bound to the neighbouring carbonyl group of the anthraquinone skeleton:



That the bonding of the metal to the phenolic hydroxyl here possesses no typical saltlike character, can be concluded from the fact that very weakly basic hydroxides are formed, or even hydrated oxides which are not more basic than those of tetravalent tin. Furthermore, even the non-metal boron can give analogous compounds. If an oxy-anthraquinone bearing a hydroxyl group in the α position is treated with boroacetic anhydride, an inner-complex compound is formed, a boroacetic ester in which the fourth co-ordination position of the boron atom is occupied by the oxygen atom of the carbonyl group (see the formula above)¹³². The formation of such inner-complex boroacetic esters can serve for the identification of α -situated hydroxyl groups in substituted anthraquinones and similarly constructed classes of compounds¹³³.

*8-hydroxyquinoline*¹³⁴ (oxine), a reagent with a manifold application giving, for example, a precipitate with zinc even at a dilution of 1 in 10⁷, likewise has the metal bound in a saltlike manner to the phenolic hydroxyl and complexly bound to the nitrogen in the adjacent ring, so that a formula diagram similar to that of the lakes arises:



8-hydroxyquinoline compound of zinc.

The oxyquinoline complexes are mostly yellow or greenish yellow. Fe^{III} gives a black, Fe^{II} a red and UO₂⁺ a reddish-brown complex.

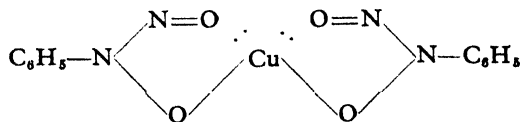
¹³² O. DIMROTH and T. FAUST, *Ber.*, 1921, **54**, 3020.

¹³³ O. DIMROTH, *Liebigs Ann. Chem.*, 1926, **446**, 97; 123.

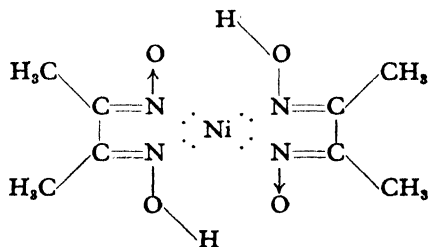
¹³⁴ F. HAHN, *Z. angew. Chem.*, 1926, **39**, 1198; R. BERG, *ibid.*, 1934, **47**, 403; *J. prakt. Chem.* 1927, [ii], **115**, 178; and in other places.

NO

Nitrosophenylhydroxylamine $C_6H_5.N.OH$, which, since it forms characteristic complexes of very low solubility with copper salts and ferric salts, bears the name *Kupferron*¹³⁵, again operates the weakly acidic hydroxyl as salt-forming and the nitroso group as complex-forming constituent:



On the other hand, in contrast to earlier views, with diacetyldioxime (dimethylglyoxime, TSCHUGAIEFF's reagent for nickel¹³⁶) in the almost insoluble (detection of 1 mg of Ni⁺⁺ in 400 ml) pinkish-red nickel complex, the nickel is bound to the nitrogen complexly as well as in a saltlike fashion. It does not replace the hydrogen in the hydroxyl of the oxime group, but that of the tautomeric nitroso form¹³⁷:



However, the "saltlike" and "complex" bonding of the nitrogen are no longer to be differentiated, since in all four co-ordination positions electron pairs effect the bond to the central nickel atom and, as the unusual insolubility of the complex indicates, the bonds are not ionizable by water.

The solubility of the deep-red ferrous complex, which on account of its colour in solution may serve as a reagent for ferrous ions, and the solubility of the cobaltous complex stand in striking contrast to the insolubility of the nickel diacetyldioxime. This difference in solubility can only be ascribable to the fact that the central atoms of the iron and cobalt complexes are hydrolyzable, but that of the nickel complex is not, since otherwise the hydrophobic nature would everywhere result in a low solubility. The hydration could proceed either through the ionization of the saltlike bonds or by direct addition of water to the central atom (see previously). Of the two possibilities, the second appears to be the more probable here, and that for the following reason.

In the inner-complex nickel diacetyldioxime, the nickel has the same co-ordination number (4) as in the very stable cyano-complex $Ni(CN)_4^{--}$.

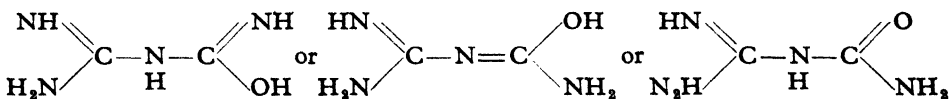
¹³⁵ O. BAUDISCH, *Chem.-Ztg.*, 1909, **33**, 1298.

¹³⁶ L. TSCHUGAIEFF, *Z. anorg. Chem.*, 1905, **46**, 144.

¹³⁷ P. PFEIFFER and J. RICHARZ, *Ber.*, 1928, **61**, 103; O. L. BRADY and M. M. MUERS, *J. Chem. Soc.*, 1930, p. 1599.

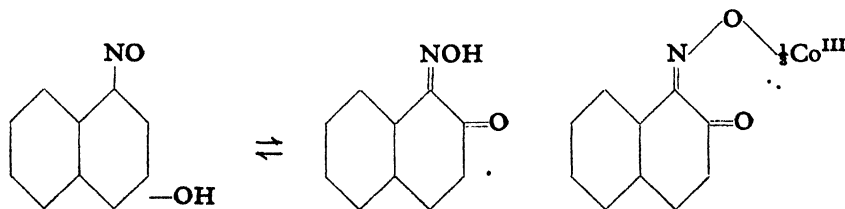
Like the latter, the diacetyldioxime-complex has a planar structure¹³⁸. This follows directly from the consideration of a model based on the classical concepts of organic chemistry concerning the structure of diacetyldioxime. The special stability of the cyano-complex is to be ascribed to a stable electronic configuration, which will be discussed in detail later (p. 397). In consequence of this, no further assumption of electrons from one of the groups is possible. For this reason, the co-ordination number of nickel in the cyano-complex $\text{Ni}(\text{CN})_4^{2-}$ is only 4, although from the purely spatial aspect, as with Fe^{II} and Co^{III} , there would be room for two further cyano groups. Similarly in nickel diacetyldioxime the acceptor powers of the nickel atom are spent, for by the inclusion of the four pairs of electrons binding the nitrogen atoms the stable electronic configuration is also attained here. The addition of water to the nickel is thereby rendered impossible. An ionizing rupture of one of the Ni—N bonds is also inconceivable, since, on account of the stability of the electronic configuration of the complex, these bonds are especially strong. In the iron and cobalt complexes, on the other hand, the stable electronic configuration does not exist. Hence water can still add on to them on both sides of the planar complex by becoming bonded to the central atom.

The same difference in solubility that occurs with the diacetyldioxime-complexes also arises with the complexes which dicyandiamidine



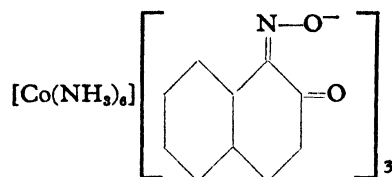
forms with nickel and cobalt. Again, in contrast to the cobalt salt, the yellow nickel complex salt is nearly insoluble. On account of the different tautomeric forms of dicyandiamidine, different formulae can be assigned to the complex, between which it has not so far been possible to decide experimentally. By analogy to the present firmly established formula of nickel diacetyldioxime, bonding of the central atom to nitrogen atoms only will also have to be assumed here, in contrast to earlier beliefs.

The case where cobalt forms a difficultly soluble inner-complex compound with a reagent while nickel gives no precipitate with the same reagent is also known, namely with α -nitroso- β -naphthol which here reacts as the tautomeric form 1:2-naphthoquinone-1-monoxime.



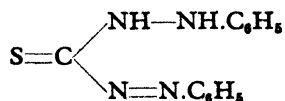
¹³⁸ L. C. PAULING, *J. Am. Chem. Soc.*, 1931, 53, 1367.

The relationships are however completely different here from those with diacetyldioxime and dicyandiamidine. In the nearly insoluble inner-complex compounds cobalt is trivalent. These are further obtained only when one commences with a compound of trivalent cobalt, that is, from hexammine cobaltic salts or similar compounds¹³⁹. A hexammine salt gives with α -nitroso- β -naphthol in sodium hydroxide solution first the dark-green salt



which at 40—50° goes over into the ammonia-free red inner-complex compound whose formula is represented on p. 145. With chloropentammine cobaltic chloride $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ the groups in the first sphere are exchanged more easily, that is, even in the cold, for the α -nitroso- β -naphthol residue. Thus the six ammonia molecules of the hexammine or the five ammonia molecules and the complexly bound chlorine, which otherwise appear to be so firmly bound, are here substituted with a remarkable ease by three α -nitro- β -naphthol molecules bound in an inner complex. The stable type of bonding of the complexes of trivalent cobalt with the electron number of krypton is thereby maintained. Divalent nickel could likewise attain the electron number of krypton in the complex if it co-ordinated with only two molecules of α -nitroso- β -naphthol. But such a complex contains the nickel, otherwise than in the stable complexes already discussed, bound to the oxygen and not to the nitrogen. In this compound, a hydrolyzing action of water on the Ni—O bond appears in consequence not to be excluded, and is even probable, since, in addition, no stable complexes of divalent nickel with the co-ordination number 4 are known in which the nickel links itself to the group by means of oxygen atoms.

Of the inner-complex compounds important in analytical chemistry, only those of *diphenylthiosemicarbazone* or *dithizone*



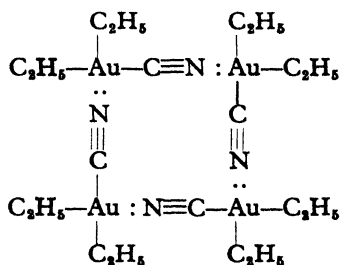
are still to be mentioned here. They are insoluble in water, but soluble in carbon tetrachloride, to which they impart characteristic colours. The solution of dithizone itself is green, that of the silver complex violet, while copper gives a yellowish brown, lead a brick red, and zinc a purplish red. On account of the intense colours of its complexes, dithizone is also very specially suited for the microchemical detection of various metals. In the complexes with the heavy metals, the very weakly acidic hydrogen atom of the NH group next to the phenyl group is replaced by the metal, while

¹³⁹ G. T. MORGAN and J. D. M. SMITH, *J. Chem. Soc.*, 1921, 119, 704.

6. Polymeric Co-ordination Compounds

As we have already ascertained on various occasions, the co-ordination number as read from the empirical formula does not always correspond to the true co-ordination number. The latter can only be derived from a consideration of the lattice if the compound is involatile. There are, however, also volatile compounds for which the molecular weight of the gaseous substance suggests that it is necessary to select a different kind of formulation from that provided by the empirical formula. Such are really to be reckoned as belonging to the polynuclear compounds and will in part be treated with these, as will aluminium chloride Al_2Cl_6 . But some of them, which stand more on their own, will receive mention here.

In diethyl gold cyanide $(\text{C}_2\text{H}_5)_2\text{AuCN}$ ¹⁴⁶, gold possesses the apparent co-ordination number 3. In reality, as a determination of the molecular weight shows, the compound is tetrameric. Hence the following formula has been assigned to it, in which the gold is linked on the one side to the carbon and on the other side to the nitrogen of different cyano groups, so that in reality it has the co-ordination number 4:



SIDGWICK and SUTTON¹⁴⁷ have suggested a similar formula, but with a cubic arrangement of the atoms, for tetrameric thallium alcoholates, *e.g.*, for the non-saltlike benzene-soluble thallium benzylate $(\text{TlOCH}_2\text{C}_6\text{H}_5)_4$ ¹⁴⁸ (Fig. 20) which melts at 74–78°. However, the stated formulae have not been subjected to detailed proof.

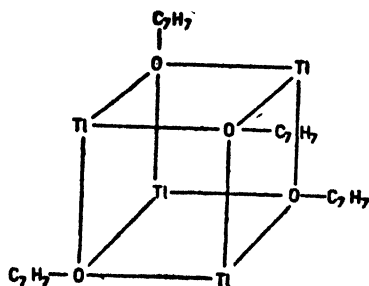
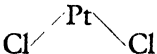


Fig. 20. Structure of the tetrameric thallium benzylate $[\text{TlOCH}_2\text{C}_6\text{H}_5]_4$.

¹⁴⁶ A. BURAWOY, C. S. GIBSON and S. HOLT, *J. Chem. Soc.*, 1935, p. 1024.

¹⁴⁷ N. V. SIDGWICK and L. E. SUTTON, *J. Chem. Soc.*, 1930, p. 1461.

¹⁴⁸ G. H. CHRISTIE and R. C. MENZIES, *J. Chem. Soc.*, 1925, 127, 2369.

On the other hand, a corresponding tetrameric structure in the lattice has been proved for the two compounds trimethyl-chloro platinum $[(\text{CH}_3)_3\text{PtCl}]_4$ and tetramethyl platinum $[(\text{CH}_3)_4\text{Pt}]_4$, both of which crystallize regularly in the space group T_d^3 ¹⁴⁹. In $[(\text{CH}_3)_3\text{PtCl}]_4$ ¹⁵⁰, the four Pt and four Cl atoms form a distorted cube whose corners they occupy alternatively. The Pt—Cl distance is 2.48 Å, that is, much too small for an ionic bond, and the  angle 99° with a distance of 3.28 Å between the chlorine

atoms. The distance between the platinum atoms, which among themselves form a regular tetrahedron, bears the value 3.73 Å. The arrangement of the carbon atoms of the methyl groups cannot be derived from interferences, but are certainly such that the methyl groups and one chlorine atom form an irregular tetrahedron about a platinum atom. In $[\text{Pt}(\text{CH}_3)_4]_4$ ¹⁵¹, the chlorine of $[(\text{CH}_3)_3\text{PtCl}]_4$ is replaced by CH_3 , whereupon the Pt—Pt distance changes to 3.44 Å. The kind of connection linking two platinum atoms is the same as that linking two aluminium atoms in the dimeric aluminium trimethyl $\text{Al}_2(\text{CH}_3)_6$ (see p. 169 ff).

Prussian Blue. — Although a plausible formulation has been possible in the examples just cited, which admittedly still require confirmation by physical methods, in the case of prussian blue, which is to be regarded as a highly polymerized compound, the position is reversed. In the attempts to find a satisfying formulation on the basis of the co-ordination theory, errors have been made on account of the lack of every kind of definite evidence. Only X-ray analysis has proved the correct means, even if it has not been able to answer all questions exhaustively.

According to the method of preparation, different kinds of prussian blue are obtained. Between the blue compounds with the old names prussian blue for that obtained from Fe^{III} and $\text{Fe}(\text{CN})_6^{\text{IV}}$ and TURNBULL'S blue for that obtained from Fe^{II} and $\text{Fe}(\text{CN})_6^{\text{III}}$ no characteristic differences have been ascertained. Analytically, the differences in the blues prepared by different methods are, on account of their partly colloidal nature, only with difficulty pinned down with any precision. Yet it appears to be certain that one has to distinguish essentially between the following compounds:

Soluble, that is, colloiddally soluble *prussian blue* containing alkali, $\text{KFe}[\text{Fe}(\text{CN})_6]$; it is formed by the action of ferrous salts on ferricyanides, as also from ferric salts and ferrocyanides, in the presence of excess of the complex cyanide.

Insoluble prussian blue, free from alkali; this is prepared in the same way

¹⁴⁹ R. E. RUNDLE and J. H. STURDIVANT, *J. Am. Chem. Soc.*, 1947, **69**, 1561.

¹⁵⁰ Preparation: Under special conditions PtCl_4 and CH_3MgI in ether and benzene give $(\text{CH}_3)_3\text{PtI}$. AgOH converts this to $(\text{CH}_3)_3\text{PtOH}$ which with HCl gives $(\text{CH}_3)_3\text{PtCl}$, insoluble in water but slightly soluble in organic solvents, more particularly benzene and chloroform (W. J. POPE and S. J. PEACHEY, *J. Chem. Soc.*, 1909, 95, 571).

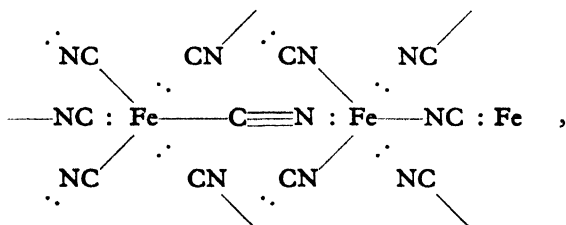
¹⁵¹ Preparation: R. E. RUNDLE, *J. Am. Chem. Soc.*, 1947, **69**, 1327.

with excess of ferric or ferrous salt respectively, or by the reduction of $\text{Fe}[\text{Fe}(\text{CN})_6]$ with hydrogen peroxide or sulphur dioxide.

White, insoluble alkali ferrous ferrocyanide $\text{K}_2\text{Fe}[\text{Fe}(\text{CN})_6]$, which is oxidized in the air.

No unequivocal proof can be obtained by chemical methods concerning whether the soluble prussian blue contains divalent iron inside and trivalent outside the complex, or *vice versa*. The means of preparation provide no certain criterion, for ferrous ion can reduce ferricyanide to ferrocyanide, being itself oxidized to ferric ion. Soluble prussian blue is decomposed by caustic soda with the formation of $\text{Fe}(\text{OH})_3$ and $\text{Na}_4\text{Fe}(\text{CN})_6$, which would speak for ferric ferrocyanide, but ammonium carbonate gives ammonium ferricyanide $(\text{NH}_4)_3\text{Fe}(\text{CN})_6$, and not $(\text{NH}_4)_4\text{Fe}(\text{CN})_6$. Likewise for insoluble prussian blue no decision can be made from its manner of formation by the reduction of $\text{Fe}[\text{Fe}(\text{CN})_6]$, since hydrogen peroxide reduces ferricyanide but not ferric ion, whereas sulphur dioxide, by contrast, is able to reduce ferric ion but not ferricyanide.

In order to understand the structure of the various kinds of prussian blue as determined by X-ray analysis¹⁵², it is best to commence with the structure of the soluble ferric ferricyanide $\text{Fe}[\text{Fe}(\text{CN})_6]$. The iron atoms, both those written as ferric ions and those bound in the complex, form a face-centred cubic lattice. It has not been possible to determine the arrangement of the cyanide ions by X-ray analysis, but illuminating assumptions concerning this point can be made. They may be supposed to link the iron atoms together in such a manner that one iron atom is linked to one side of the carbon — the normal bond of complex iron cyanides — and another iron atom linked to the other side of the nitrogen. The cyano groups here play the same rôle as has been ascribed to them in diethyl-cyano gold, except that, on account of the co-ordination number 6 of the iron, a three-dimensional network is here formed according to the scheme



and likewise, as shown here for the central group, for every cyano group. If this conception is transferred to the lattice structure, a cyanide ion is allocated to the middle of each edge of an elementary cube formed from iron atoms with an edge 5.1 Å long, so that a perovskite structure (p. 128)

¹⁵² J. F. KEGGIN and F. D. MILES, *Nature*, 1936, **137**, 577. The structures of other more complex ferro- and ferricyanides: R. RIGAMONTI, *Gazz. chim. ital.*, 1937, **67**, 137; 146; 1938, **68**, 809; H. B. WEISER, W. O. MILLIGAN and † B. BATES, *J. Phys. Chem.*, 1938, **42**, 945; A. K. VAN BEVER, *Rec. trav. chim. Pay Bas*, 1938, **57**, 1259.

occurs in the lattice of $\text{Fe}[\text{Fe}(\text{CN})_6] = 2\text{Fe}(\text{CN})_3$, in which the centres of the elementary cubes are unoccupied (Fig. 21), as with rhenium trioxide ReO_3 .

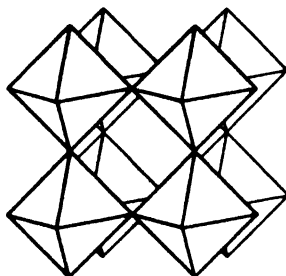


Fig. 21. Co-ordination octahedra of ferric ferricyanide $\text{Fe}[\text{Fe}(\text{CN})_6]$. Basic structure of prussian blue. Simultaneously the lattice type of rhenium trioxide.

This network, in which the trivalent iron atoms are octahedrally surrounded by six cyano groups, like the titanium atoms by oxygen atoms in perovskite, is uncharged. From it are derived the various other complex ferri-ferrocyanides through the iron atoms being not all trivalent, whereby the whole network assumes a negative charge and becomes an ionic scaffolding. According to the number of divalent iron atoms, the centres of a proportion of the elementary cubes become occupied by cations compensating the negative charge, as does the TiO_6 octahedral network of perovskite by calcium. These cations in the centres of the elementary cubes have the co-ordination number 12 relative to the cyano groups, like calcium towards oxygen in perovskite.

Thus, from the network of $\text{Fe}[\text{Fe}(\text{CN})_6]$, that of soluble prussian blue $\text{KFeFe}(\text{CN})_6$ is derived in the following manner. The iron atoms it contains are alternatively di- and trivalent, so that altogether a lattice complex with the structural unit $[\text{Fe}^{\text{III}}\text{Fe}^{\text{II}}(\text{CN})_6]'$ bearing one negative charge per unit results. Since twice as many iron atoms are present as there are alkali ions, a potassium ion is found in every second cube of iron atoms. The white compound $\text{K}_2\text{Fe}[\text{Fe}(\text{CN})_6]$, containing only divalent iron, is derived from the anionic lattice complex $[\text{Fe}^{\text{II}}\text{Fe}^{\text{II}}(\text{CN})_6]''$ and contains an alkali atom in each cube. The alkali-free prussian blue can be comprehended either as the ferric compound of the anionic lattice complex $[\text{Fe}^{\text{III}}\text{Fe}^{\text{II}}(\text{CN})_6]'$ and accordingly written $\text{Fe}^{\text{III}}[\text{Fe}^{\text{III}}\text{Fe}^{\text{II}}(\text{CN})_6]_3$, or as the ferrous compound of the same complex and written $\text{Fe}^{\text{II}}[\text{Fe}^{\text{III}}\text{Fe}^{\text{II}}(\text{CN})_6]_2$. Perhaps the first arises as prussian blue from Fe^{III} and $\text{Fe}(\text{CN})_6^{\text{IV}}$, and the second as TURNBULL'S blue from Fe^{II} and $\text{Fe}(\text{CN})_6^{\text{III}}$. Yet, as already emphasized, it is not decided whether the two substances are different.

The special kind of linking in the lattice complex, as is brought about here between the iron atoms by the cyano groups, is named *supercomplex-formation*.

A supercomplex of the same type as prussian blue occurs in the red-brown

cupric ferrocyanide. In this the divalent iron of the $[\text{Fe}^{\text{II}}\text{Fe}(\text{CN})_6]''$ complex which is linked to the nitrogen is to be thought of as replaced by divalent copper. Alkali-containing cupric ferrocyanide must accordingly be written $\text{K}_2[\text{CuFe}(\text{CN})_6]$ and not $\text{K}_2\text{Cu}[\text{Fe}(\text{CN})_6]$. The copper is not present in the cation like the alkali, but is enmeshed in the complex. The alkali-free cupric ferrocyanide $\text{Cu}_2\text{Fe}(\text{CN})_6$ is not a salt corresponding to the alkaline-earth ferrocyanides $\text{Ca}_2[\text{Fe}(\text{CN})_6]$, but is the supercomplex copper compound $\text{Cu}[\text{CuFe}(\text{CN})_6]^{153}$. In order to indicate their highly polymerized nature, all these supercomplexes should really be written in the following manner: $[\text{Fe}^{\text{III}}\text{Fe}^{\text{II}}(\text{CN})_6]_n^{2n-}$, $[\text{Fe}^{\text{II}}\text{Fe}^{\text{II}}(\text{CN})_6]_n^{2n-}$, $[\text{CuFe}(\text{CN})_6]_n^{2n-}$ and, by way of example, the last-named copper compound $\text{Cu}_n[\text{CuFe}(\text{CN})_6]_n$.

Like the iron, the copper in these supercomplexes has the co-ordination number 6. Whether it is admissible for the insoluble ferrocyanides of other elements, on account of the different co-ordination numbers usually shown by the latter, to assume rather different formulations¹⁵⁴ appears to be very questionable¹⁵⁵.

In the crystal structure of the insoluble cyano-complexes of iron, the $\text{Fe}(\text{CN})_6$ octahedra, which are isolated in the soluble potassium ferrocyanide, are recognizable, but with their corners firmly interlinked via the cyano groups which bind the supercomplex together. It is very remarkable that in the soluble ferric ferricyanide $\text{Fe}[\text{Fe}(\text{CN})_6] = 2\text{Fe}(\text{CN})_3$ the same supercomplex structure exists, but here is easily broken up by water into the ions Fe^{III} or $\text{Fe}(\text{OH})_2^{\text{III}}$ and $\text{Fe}(\text{CN})_6^{\text{III}}$. The WERNER complex formula $\text{Fe}[\text{Fe}(\text{CN})_6]$ provides this behaviour on solution but, on the contrary, no correct picture of the crystal structure, for the latter does not contain two different kinds of trivalent iron, one cationic and the other bound complexly in the anion. Rather all of the iron atoms are structurally equivalent, so that here the simple formula $\text{Fe}(\text{CN})_3$ or $[\text{Fe}(\text{CN})_3]_x$, analogous to ReO_3 or $(\text{ReO}_3)_x$ respectively, appears to be fitting. The supercomplex structure becomes stable towards the ionizing action of water only when, as a consequence of the divalence of the iron atoms, the inclusion of cations at the centres of the elementary cubes results.

The supercomplex structures, like the polymeric co-ordination compounds, are strictly to be reckoned as polynuclear complex compounds. Likewise, according to their lattice structure, various salts containing water of crystallization also belong there, like the already discussed $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$, as

¹⁵³ Regarding the isomorphism of $\text{Cu}_2\text{Fe}(\text{CN})_6$ with $\text{Co}_2\text{Fe}(\text{CN})_6$, $\text{Ni}_2\text{Fe}(\text{CN})_6$, $\text{Mn}_2\text{Fe}(\text{CN})_6$, see H. B. WEISER, W. O. MILLIGAN and J. B. BATES, *J. Phys. Chem.*, 1938, 42, 945.

¹⁵⁴ H. J. EMELÉUS and J. S. ANDERSON, *Modern Aspects of Inorganic Chemistry*, p. 140 (Routledge, London, 1938).

¹⁵⁵ In particular it is not apparent why the zinc (*loc. cit.*) is allowed only the co-ordination number 4, which it doubtless possesses in $\text{Zn}(\text{CN})_4^{\text{II}}$, whereas it nevertheless has the co-ordination number 6 in $\text{Zn}(\text{NH}_3)_6^{\text{II}}$. The co-ordination number 6 assumed for Cu^{II} in the supercomplex is by no means the rule, it being rather that in the cyano-complex, namely 4, than that of the ammine-complex.

well as non-electrolytes such as $\text{Cl}_2\text{Cd}(\text{NH}_3)_2$, which in the lattice really represent complex compounds of infinitely many nuclei. The principles governing the structure of polynuclear complex compounds will now be illustrated for complex salts containing more than one central atom, beginning with the dinuclear complexes.

PART II. POLYNUCLEAR COMPLEX COMPOUNDS

1. Dinuclear Compounds

A transcendent position within a complex need not always be assumed by only one atom as the central atom. There may also be several of them. Such compounds which contain several central atoms are called *polynuclear compounds*. The simplest and longest-known cases occur in the anions of the pyro-acids $\text{S}_2\text{O}_7^{2-}$, $\text{Cr}_2\text{O}_7^{2-}$, $\text{P}_2\text{O}_7^{4-}$. But the theory of the structure of polynuclear compounds was not developed through these; indeed, their structure was in fact for a long time disputed¹. The structure of polynuclear compounds is best derived from the spatial structure of mononuclear compounds in which the polyhedra representing them are allowed to contact one another firstly by corners, secondly by edges, and thirdly by faces². The two central atoms are then bound respectively by one, two or three atoms or groups of atoms, termed *bridges*, provided the polyhedra are also based on the most frequent co-ordination numbers, 4 and 6, corresponding to tetrahedra or octahedra (Fig. 22).

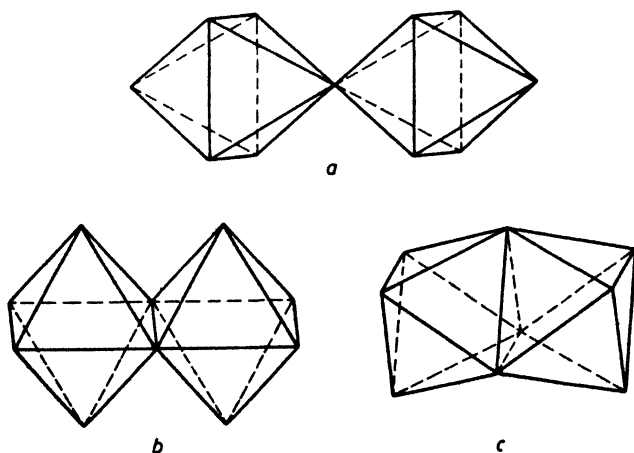


Fig. 22. Bridge-formation in polynuclear compounds with co-ordination number 6. Octahedra which are in contact at (a) a corner, (b) an edge, (c) a face.

¹ A. WERNER, according to R. F. WEINLAND's *Einführung in die Chemie der Komplexverbindungen*, p. 292 (1919); 2nd Ed., p. 451 (1924).

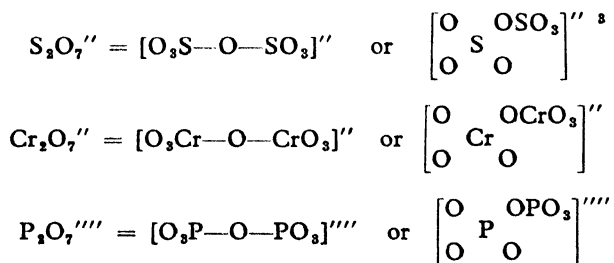
² Cf. G. WITTIG, *Stereochemie*, pp. 270—271 (Leipzig, 1930).

With the cube, which corresponds to the co-ordination number 8 — in $\text{Mo}(\text{CN})_8$ '''' the co-ordination number 8 has another arrangement (p. 138) — contact by means of two surfaces would mean four bridges, but such a fourfold bridge has not yet been observed. The different ways of joining tetrahedra and octahedra correspond to the method of VAN 'T HOFF for illustrating double and triple bonds by placing two carbon tetrahedra together. But an essential difference exists, inasmuch as the corners of VAN 'T HOFF's tetrahedra are not occupied, the "bends" in the valencies when edges or faces are in contact having, of course, no real meaning, whereas in the polynuclear compounds an atom or atomic grouping is situated in each case at the corners in contact. Through these the central atoms are indirectly linked, and not directly like the carbon atoms in VAN 'T HOFF's case. Proof of the correct nature of the conception of the spatial structure of polynuclear compounds developed here will be given for individual examples.

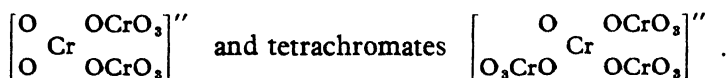
Without first going into the kind of link effected by the bridge atoms, a series of examples of dinuclear compounds with one, two and three bridge atoms or groups of atoms will be cited. The bridge will be denoted in the nomenclature by means of the letter μ .

(i) Dinuclear Compounds with a single Bridge Atom

Anions of pyro-acids are examples of the addition of an acid anhydride to the parent ion:



Multinuclear isopoly-acid anions can also be derived according to the same scheme, for example the trichromates



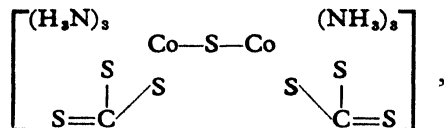
For further, see p. 180.

Non-electrolytes :

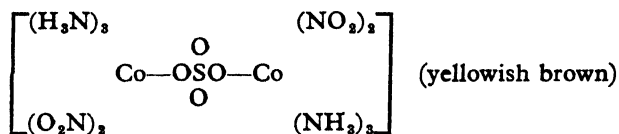
In μ -sulpho-bis-trithiocarbonato-di-triammine cobalt ⁴

³ G. HÄGG accepts this structure as to a certain extent self-evident without proof by X-rays: *Z. physik. Chem.*, 1932, **B 18**, 211. $\text{S}_2\text{O}_7''$, on the contrary, = $[\text{O}_3\text{S}-\text{SO}_3]''$ according to ZACHARIASEN (see p. 127, footnote 73).

⁴ K. A. HOFMANN, *Z. anorg. Chem.*, 1897, **14**, 263.



the trithiocarbonato groups occupy two co-ordination positions. The compound is prepared from $\text{Co}(\text{OH})_2$ plus NH_3 and CS_2 under the oxidizing action of atmospheric oxygen. It forms lustrous black rhombohedra which dissolve in water to give a yellowish-brown coloration. The divalent thiosulphate ion $\text{S}_2\text{O}_3^{2-}$ can take the place of the divalent sulphur forming the bridge. Also known are analogously built complexes with the sulphate ion SO_4^{2-} as bridge, like μ -sulphato-di-dinitro-di-triammine cobalt:

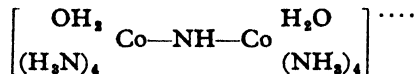


Cations:

Examples are the violet-red decammine- μ -oxo-dichromic ion

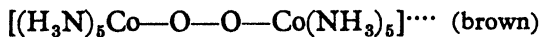


(see also later under decammine- μ -ol-dichromic ion) and the diaquo-octammine- μ -imino-dicobaltic ion ⁵

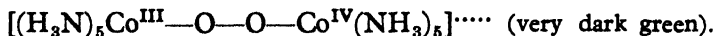


The latter ion is interesting because stereoisomerism has been ascertained for it, this depending on the fact that the two water molecules can take up the edgewise as well as the diagonal positions with respect to the bridge imino group ⁶.

The peroxo-compounds contain two bridge atoms, *e.g.*, the decammine- μ -peroxo-cobaltic ion



It is the first oxidation product of ammoniacal cobaltous solutions. The oxidation can also proceed still further and lead to a dinuclear compound with a peroxo bridge in which tetravalent cobalt must be assumed, because the charge on the complex is one unit higher:



The bridges so far discussed come into existence collectively, so that the central atom at each end of the bridge, like the bridge atom, contributes one valence electron to the bond. Thus an electron-pair bond arises at each end, that is, in the old terminology of WERNER, only principal valencies are operative. But if the bridge-forming atoms possess lone electron pairs, bridges may also arise in which the two electrons necessary for each bond

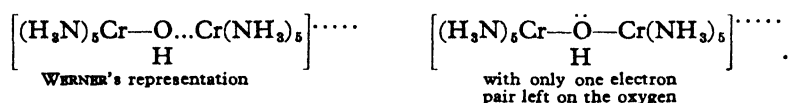
⁵ A. WERNER and A. BASELLI, *Z. anorg. Chem.*, 1898, **16**, 150.

⁶ A. WERNER, *Ber.*, 1907, **40**, 64; 65; G. WITTIG, *Stereochemie*, p. 271.

are provided by these lone electron pairs. In the older terminology, the bridge atom then operates a principal valency on the one side of the bridge and a subsidiary valency on the other. The bonds, however, are as little to be differentiated from one another as are the four N—H bonds in the ammonium ion. The dissymmetry in the formulae of these compounds present in the old manner of writing them is thus not real. Today the same valence-line must instead be written on both sides of the bridge, at the same time withdrawing a lone pair of electrons from the atom in the bridge. It seems questionable, however, whether this manner of representation reflects the correct distribution of electrons. The charges of these complexes are reckoned from the sum of the charges of the two central atoms, less the charge of the bridge-building group which it would possess as an independent ion (OH', NH₂').

Examples of such compounds containing a hydroxyl group as the bridge, abbreviated to *ol*, are:

The decammine- μ -*ol*-dichromic ion (red)



The bromide is prepared from an ammoniacal solution of chromous bromide by oxidation with oxygen.

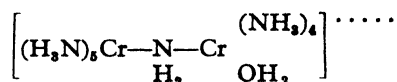
Bridge-forming *ol* groups can invariably be differentiated from hydroxo groups bound complexly in the first sphere of basic salts, by the fact that they do not react with acids to form aquo groups.

Here the oxygen has the co-ordination number 3 as in the oxonium compounds. But in contrast to the latter, the hydrogen of the bridge hydroxyl is *not ionic*, the solutions of these so-called *rhodo-chromic salts* having a *neutral* reaction. Isomeric compounds, the carmine-red *erythro-chromic salts* can be obtained from them. These have a strongly acidic reaction. An explanation for the nature of the isomerism between the rhodo and erythro salts for a long time caused chemists to rack their brains, once the original explanation of WERNER as a valence isomerism was recognized to be impossible, since here a differentiation was made between principal- and subsidiary-valence bonding in an onium compound⁷ — which otherwise, even according to WERNER, was not permissible. Not until 1937 was proof obtained by K. A. JENSEN^{7a} that only the rhodo-chromic salts possess the foregoing constitution and that, by contrast, the erythro-chromic

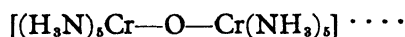
⁷ According to this, the H and one Cr atom in the rhodo salts were each supposed to be bound by principal valencies, and the other Cr atom by a subsidiary valency to the O atom, whereas in the erythro salts both Cr atoms were supposed to be bound by principal valencies and the H atom by a subsidiary valency. Isomerism of this or a similar kind, which A. R. HANTZSCH (*Ber.*, 1919, 52, 1535) believed he had established for pyroxonium and pyridonium compounds, among others, later found another explanation (A. R. HANTZSCH and A. BURAWOY, *ibid.*, 1932, 65, 1059).

^{7a} K. A. JENSEN, *Z. anorg. Chem.*, 1937, 232, 257.

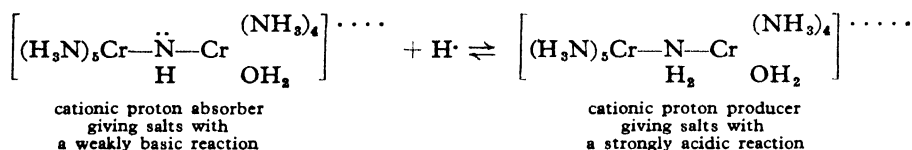
salts contain one amino group as bridge and also an aquo group:



Exchange of the bridge arises in the action of ammonia on the rhodo salt, which first produces blue "basic" salts, preferably the basic dithionate or bromide. The ammonia extracts the proton from the ol bridge and leaves a tetravalent cation:



The strongly alkaline reaction of solutions of these salts is readily understandable, since the oxygen of the oxo bridge has a tendency to take up a proton from the water. The solutions change rapidly and become carmine red in colour. Basic erythro salts — which have an only very weakly alkaline reaction, however — are thereby formed as a result of the exchange of O for NH. With acids, these give the normal — but in reaction strongly acidic — erythro salts:



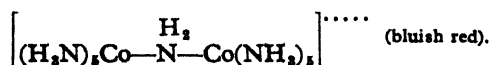
By splitting off one equivalent of acid, the violet-red decammine- μ -oxo-dichromic salts (p. 156) are formed from the erythro salts through a further exchange of bridge atoms.

In X-ray structure analysis by the DEBYE-SCHERRER method, the corresponding isomeric rhodo- and erythro-chromic salts provide the same X-ray diagram. The salts are thus isomorphous with one another, which is to be expected where solely groups or molecules with the same number of electrons substitute one another.

For compounds in which an *amino group* forms the bridge, the same holds true in principle as for the compounds with ol bridges. Here also with the help of the lone electron pair on the nitrogen — or in the old formulation by using principal and subsidiary valencies — it is possible to give expression without difficulty to the linking of the two central atoms through the bridge. Even if also for compounds with an amino bridge no facts are as yet known which speak against this formulation, nevertheless, by reason of the analogy with the ol bridges, it may be doubted whether they reproduce correctly the operation of the bonding electrons.

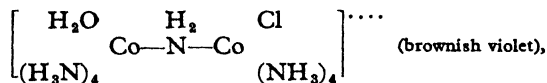
Examples of compounds with an amino group are:

The decammine- μ -amino-dicobaltic ion which, analogous to the decammine- μ -ol-dichromic ion, can be written



It is prepared from octammine- μ -amino-ol dicobaltic nitrate, a compound containing OH and NH₂ bridges (see p. 160).

The chloro-aquo-octammine- μ -amino-dicobaltic ion ⁸



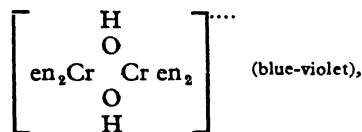
which is prepared by oxidizing an ammoniacal solution of cobaltous nitrate with atmospheric oxygen at 30°, neutralizing with sulphuric acid, treating the brownish-black inhomogeneous so-called VORTMANN'S sulphate which separates out with concentrated nitric acid and dissolving out one of the salts — this being green and containing one NH₂ and one peroxo group as bridges. The remaining red octammine- μ -sulphato-amino cobaltic nitrate, which contains one NH₂ and one sulphato group as bridges, is treated with concentrated hydrochloric acid to give the chloride of the required ion.

(ii) Dinuclear Compounds with two Bridge Atoms

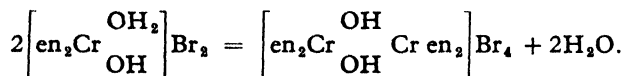
With these compounds some but not all combinations of bridges occurring in the linking of nuclei by a single bridge are possible. Especially frequent is the occurrence of two ol bridges, as well as the combination of amino and ol bridges, and also of amino and peroxo groups. As bridge components, sulphato, nitrate and nitro groups can also co-operate, as well as relatively rarely an oxygen atom and an amino group. Of the complex compounds which belong here, those of chromium, which invariably appears in them as trivalent, have been thoroughly investigated, as well as those of cobalt, which is mostly trivalent but can also occur as tetravalent on one side of a peroxo bridge.

Example of *two ol bridges*:

The tetrakis-ethylenediamine- μ -diol-dichromic ion



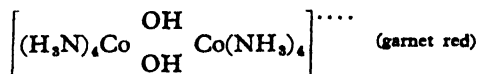
the bromide of which is prepared from the red *cis*-hydroxo-aquo-bis-ethylenediamine chromic bromide by heating it dry:



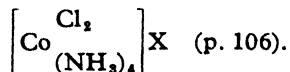
It is characteristic that the cleavage of water and formation of two ol bridges succeeds only with the *cis* or edgewise configuration of the OH and H₂O. This is a proof of the appropriateness of the conception that in compounds with two bridges the octahedra are to be thought of as placed with their edges together. In this manner, the structure of the foregoing compound is illustrated directly.

⁸ A. WERNER, *Liebigs Ann. Chem.*, 1910, **375**, 44.

Conversely the cleavage of the octammine- μ -diol-dicobaltic ion

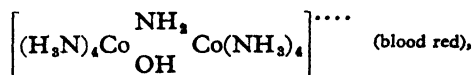


with strong hydrochloric acid, which leads to the violeo-cobaltic ion, provides a proof for the *cis* configuration of the violeo salts

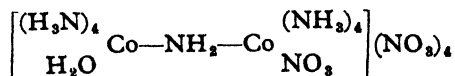


Examples of *one ol and one amino bridge*:

The octammine- μ -amino-ol-dicobaltic ion ⁹

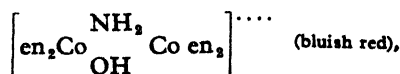


the chloride of which is prepared by the removal of hydrogen chloride from the violet-brown chloro-aquo-octammine- μ -amino dicobaltic chloride in aqueous solution. The constitution has been proved in the following manner. Cleavage with concentrated hydrochloric acid in strong sulphuric acid solution gives a mixture of dichloro-tetrammine cobaltic chloride and ^achloro-pentammine cobaltic chloride. In the latter, the five nitrogen atoms remain on one of the two central atoms, while the former originates from the other half, from which the NH_2 has detached itself. The co-ordination position which has thus been freed is replaced by a chlorine atom, and the hydroxyl group by a second chlorine atom. The formulation with an imino group and a water molecule of crystallization is not permissible, firstly because a molecule of water cannot be removed from the complex, secondly because the reactions of an imino group have not been demonstrated, and thirdly because the cobalt would thereby have the co-ordination number 5 instead of 6. As far as the salts, like the chloride, for example, crystallize with water of crystallization, the number of water molecules corresponds to the number of the anions, that is, four for the chloride, and not five, as a formula with an imino bridge and without an ol bridge would demand. The nitrate crystallizes without water of crystallization. From it, by unilateral rupture of the bridge on the side of the ol group, octammine- μ -amino-nitrato-aquo dicobaltic nitrate



is obtained, and from this decammine- μ -amino dicobaltic nitrate (see above) with liquid ammonia.

In the example of the tetrakis-ethylenediamine- μ -amino-ol-dicobaltic ion ¹⁰,

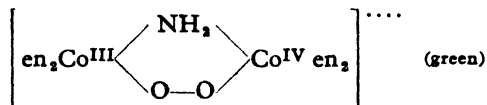


⁹ A. WERNER, *Liebigs Ann. Chem.*, 1910, **375**, 44.

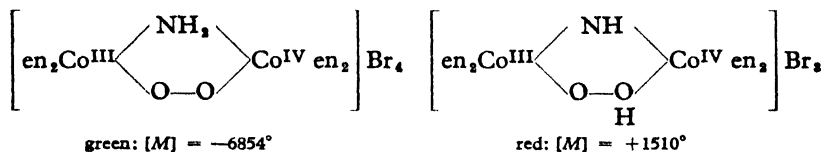
¹⁰ A. WERNER, *Ber.*, 1914, **47**, 1977—1978.

the spatial structure, as reproduced by two octahedra in contact at one edge, has been proved by preparation of the optical enantiomorphs. These were obtained by reduction of the enantiomorphs of the tetrakis-ethylenediamine- μ -amino-peroxo-cobalt-III-cobalt-IV ion¹¹. They were separated by crystallization of the bromocamphorsulphonate.

The last-named is an example of the combination of *amino and peroxo bridges*:

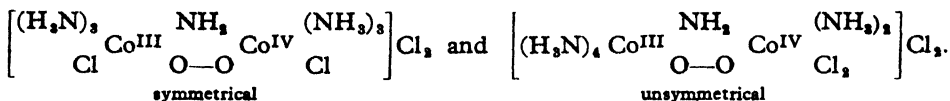


Here, again, in the salts the same isomerism is known that has already been mentioned as "valence isomerism" in the case of the rhodo- and erythrochromic salts. In the old symbolism, the green and the isomeric red forms are distinguished in that in the green a cobalt atom, whereas in the red a hydrogen atom (or HX), appears to be bound by means of a subsidiary valency on the nitrogen. According to JENSEN (p. 157), however, this isomerism is also a structural isomerism:



Against the older formulation of WERNER, the same objections can be raised as formerly (p. 157): that of JENSEN reproduced here is however correct. It is noteworthy that the red oxonium form rotates the plane of polarized light in a direction opposite to that of the green form with the amino group as bridge.

For the amino-peroxo-bridge complexes an isomerism is also known, which is to be attributed to a different distribution of the same groups about the two central atoms, and can be denoted as position isomerism:

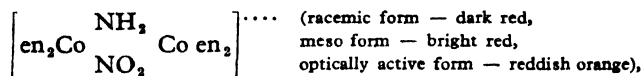


Dichloro-hexammine- μ -amino-peroxo cobalt-III cobalt-IV chloride is green. The constitutional proof was accomplished for the unsymmetrical salt — similarly to that for the octammine- μ -amino-ol-cobaltic ion — by cleavage with concentrated hydrochloric acid, when chloro-pentammine cobaltic chloride results. The five nitrogen atoms stay put on the left-hand cobalt atom, while chlorine becomes bound in the first sphere in place of the oxygen of the peroxo group.

For the combination of *amino and nitro* groups as bridge groups, in the tetrakis-ethylenediamine- μ -amino- μ -nitro-dicobaltic ion¹²

¹¹ A. WERNER, H. KUH and P. WÜST, *Ber.*, 1914, **47**, 1961.

¹² A. WERNER, E. BINDSCHEDLER and A. GRÜN, *Ber.*, 1907, **40**, 4834.

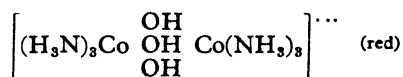


which can be obtained from the corresponding peroxo compound (see p. 161) and nitrous acid, not only have the optical enantiomorphs and the racemate been obtained, but also a non-resolvable meso form. The symmetry relationships correspond perfectly to the tartaric acid type. The optically active salts revert to the meso form on evaporation.

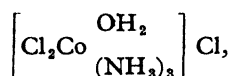
(iii) Dinuclear Compounds with three Bridge Atoms

Three ol bridges:

The hexammine- μ -triol-dicobaltic ion ¹²

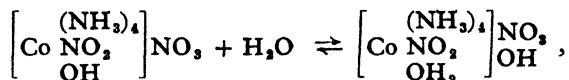


is readily formed by various paths from triammine-cobaltic salts containing at least one aquo group, *e.g.*, by the action of caustic soda on dichloro-aquo-triammine cobaltic chloride

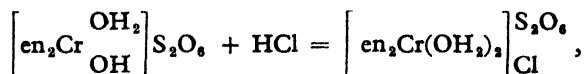


or by warming chloro-bromo-aquo-triammine cobaltic chloride to 60° with a little water, and by other methods.

The constitutional proof has been accomplished by cleavage with hydrochloric acid, which yields triammine-cobaltic salts quantitatively, *e.g.*, with hydrochloric acid the same dichloro-aquo chloride as that from which the dinuclear triol compound can be obtained with alkali. The OH groups do not occur as hydroxo groups, since then the salts would *either* react alkaline analogously to hydroxo-nitro-tetrammine cobaltic nitrate,



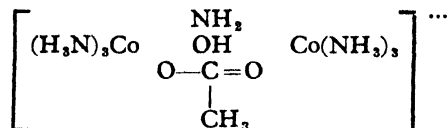
which they do not — their aqueous solutions have a neutral reaction — or on treatment with acids the hydroxo groups would be replaced by aquo groups in analogy, by way of example, to the hydroxo-aquo-bis-ethylenediamine-chromic salts (cf. p. 159),



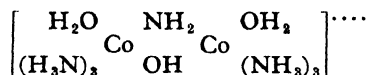
which likewise does not occur.

Three different bridges — ol, amino and acetato — are contained by the hexammine- μ -amino-ol-acetato-dicobaltic ion

¹² A. WERNER, E. BINDSCHEDLER and A. GRÜN, *Ber.*, 1907, 40, 4834.



It is formed very easily from a compound containing the doubly bridged diaquo-hexammine- μ -amino-ol-dicobaltic ion



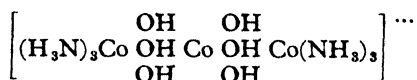
and dilute acetic acid.

2. Tri- and Tetranuclear Compounds

(i) Trinuclear Compounds

The kinds of bridge links in trinuclear compounds are the same as in the dinuclear. A few examples will serve to illustrate this.

The hexammine- μ -hexol-tricobaltic ion¹³



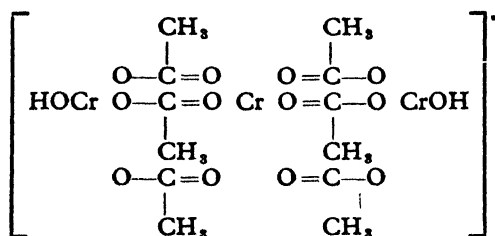
corresponds to the hexammine- μ -triol-dicobaltic ion, except that here three octahedra are to be thought of as making contact by means of two faces, instead of two octahedra with one face in common.

The trinuclear acetato-complexes of trivalent metals are very varied and especially important analytically. Of these a dark brownish-red ferric complex obtained in the 'acetate method' is hydrolytically cleaved by boiling. Besides acetato groups, hydroxo groups are also contained in them. In the case of chromium, the place of the acetic acid residue may be taken by those of other fatty acids from formic acid onwards, and likewise by the residues of some aromatic acids, such as benzoic acid. The triferric complexes are less stable than the corresponding complexes of chromium, but, apart from that with acetic acid, complexes are known with various aromatic acids, *e.g.*, benzoic acid, α -naphthoic acid and cinnamic acid. There are no genuine ferric salts of organic carboxylic acids, like $\text{Fe}(\text{CH}_3\text{COO})_3$; generally triferic-hexacido-complexes occur if anionic complexes are not formed, like $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ (green) with oxalic acid or $[\text{Fe}(\text{HCOO})_6]^{3-}$ (pale green) with formic acid. Hexaquo-ferric salts of organic acids are unknown. On the other hand, the corresponding hexaquo-chromic salts are familiar, *e.g.*, the violet hexaquo chromic acetate $[\text{Cr}(\text{OH}_2)_6](\text{CH}_3\text{COO})_3$, which arises on dissolving freshly precipitated chromic hydroxide in acetic acid at ordinary temperatures. But on dissolving in the warm, green salts which are derivatives of trichromic-acetato-complexes are formed. Formerly, on account of their empirical formulae, for example, $\text{Cr}_3(\text{CH}_3\text{CO}_2)_7(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ (with only one CH_3COO group ionic), they were designated as basic chromic acetates. Such complexes

¹³ A. WERNER, *Liebigs Ann. Chem.*, 1910, **375**, 140.

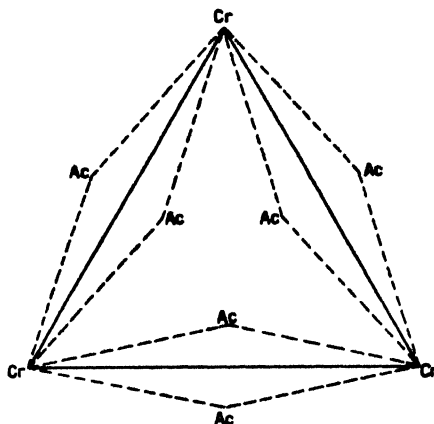
also arise on reducing chromic acid by commercial acetic acid (the pure acid does not react). No less than 17 chromic acetates are known in all. The structure of the complexes is not yet known with certainty in every case. In particular, there is still uncertainty in various cases whether the hydroxyl radicals are hydroxo groups or form bridges as ol groups. Ammonia and pyridine can also be introduced into the complexes which usually retain six acetato groups.

The *hexacetato-dihydroxo-trichromic complex*, which is contained in the forementioned salt $\text{Cr}_3(\text{CH}_3\text{COO})_7(\text{OH})_2 \cdot 4\text{H}_2\text{O}$, apparently has the following symmetrical constitution:



It can be thought of as constructed from an octahedron containing the middle chromium atom as central atom, and two tetrahedra joined on to opposite faces of the octahedron. The dissimilarity appearing in the formula between the two oxygen atoms of the acetato group — hydroxyl and carbonyl oxygen — is not to be considered as real, since in the acetato group, just as in the anion of every carboxy-acid, the bonding electrons containing these oxygen atoms distribute themselves equally between the two oxygen atoms, so that they are no longer distinguishable (mesomerism — see Chapter VI, p. 424 ff).

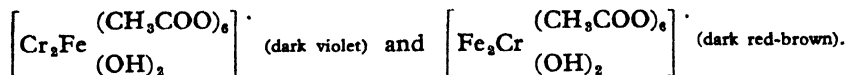
A ring structure has however been suggested, in which the chromium atoms are bound to one another by only two acetato bridges according to the scheme¹⁴:



¹⁴ A. HENRICHSEN, cited by R. F. WEINLAND in *Einführung in die Chemie der Komplexverbindungen*, pp. 398—399 (2nd Ed., 1924).

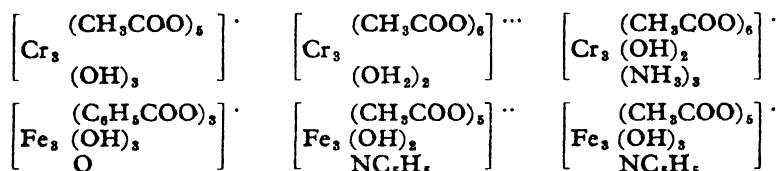
But it is then not easy to understand why only two hydroxyl radicals should be found inside this complex.

Mixed acetato-complexes of this kind containing trivalent chromium and trivalent iron as central atoms are also known, *e.g.*,



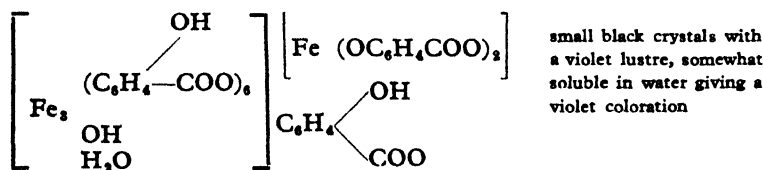
They are obtained when $\text{Cr}(\text{OH})_3$ and $\text{Fe}(\text{OH})_3$ in the molecular ratios 2 : 1 and 1 : 2 respectively are dissolved by warming in glacial acetic acid. Their formation is the reason why the acetate method breaks down with the simultaneous presence of iron and chromium, since they are not hydrolyzed by boiling with water, so that invariably only a part of the iron or chromium respectively, that which is not converted to a mixed complex, succeeds in being separated as hydrated oxide.

The following small selection may witness to the variety of the trinuclear complexes which belong here:



Most of the ferric acetato-complexes containing pyridine, however, are tetranuclear.

There are especially interesting complexes of trivalent iron, which arise by the association of a trinuclear hexacido-complex with a complex anion of trivalent iron. Such salts are formed with salicylic acid¹⁵, *e.g.*, [hexasalicylato-hydroxo triferric] [disalicylatoferrite] salicylate :



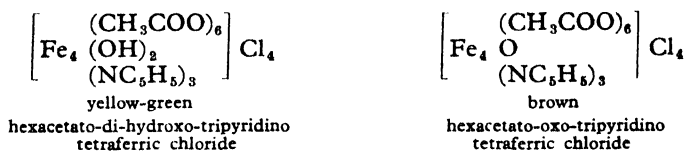
The violet-blue ferric chloride reaction with salicylic acid depends upon the formation of such salts.

(ii) Tetranuclear Compounds

Compounds containing four or more nuclei offer nothing fundamentally new in principle with respect to the di- and trinuclear compounds. Consequently, it may suffice to mention a few of the compounds which, taken as a whole, are now known to be very numerous.

¹⁵ R. F. WEINLAND and A. HERZ, *Liebigs Ann. Chem.*, 1913, **400**, 235; R. F. WEINLAND and K. ZIMMERMANN, *Arch. Pharm.*, 1917, **255**, 204.

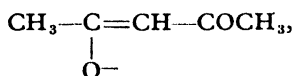
*Ferric-acetato-pyridino salts*¹⁶ :



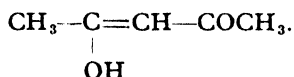
*Ferric-acetylacetonone-pyridino salts*¹⁷ :



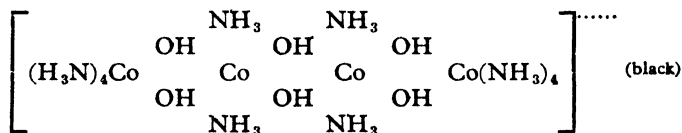
The abbreviation 'acac' signifies the residue of the acetylacetonone molecule in the enol form



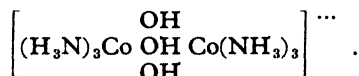
and 'acacH' a molecule of acetylacetonone in the enol form



The *dodecammine-μ-hexol-tetracobaltic ion*



is interesting because it is a dimer of the hexammine-μ-triol-dicobaltic ion¹⁸



Concerning the spatial structure of the tetranuclear complexes and, in addition, various trinuclear complexes, H. REIHLEN has developed plausible ideas on the basis of the octahedral model, to which reference only is made here¹⁹. Structural confirmation by X-ray investigation is still lacking. But a very strong support for these views may well be seen in the lattice structures of compounds such as $\text{Cl}_2\text{Cd}(\text{NH}_3)_2$ (pp. 122, 123).

3. Polynuclear Halides with Halogen Bridges

(i) Aluminium Halides

The conception that bridge atoms effect the link between two nuclei has been employed with success for explaining the abnormal molecular

¹⁶ R. F. WEINLAND and C. BECK, *Z. anorg. Chem.*, 1913, **80**, 402.

¹⁷ R. F. WEINLAND and E. BÄSSLER, *Z. anorg. Chem.*, 1916, **96**, 109.

¹⁸ A. WERNER, *Ber.*, 1907, **40**, 4836.

¹⁹ *Ueber die räumliche Bedeutung der Koordinationszahl bei mehrkernigen Verbindungen*, *Z. anorg. Chem.*, 1920, **114**, 65.

weight of some halides, namely of the dimeric aluminium and ferric halides (ferric iodide does not exist), and also of the trimeric molybdenum dichloride and dibromide. In the case of the first-named compounds, the molecular weight has been ascertained by vapour-pressure determinations at not too high temperatures, that is, up to about 500°. In the case of the trimeric molybdenum dichloride Mo_3Cl_6 , boiling-point elevation in ethyl alcohol has been employed²⁰. For the latter halide, various chemical reactions also indicate the threefold formula. The relationships in the aluminium and iron halides will be discussed in detail first.

Even before the double formulae for AlCl_3 and FeCl_3 had been demonstrated by determinations of the molecular weight, the adherents of constant valency had formulated these compounds as dimers with tetravalent metal atoms analogously to ethane with tetravalent carbon, that is, with Al—Al and Fe—Fe bonds: $\text{Cl}_3\text{Al—AlCl}_3$; $\text{Cl}_3\text{Fe—FeCl}_3$. If one also wrote ferrous chloride as a dimer with a double bond analogous to ethylene, $\text{Cl}_2\text{FeFe=Cl}_2$, the iron was constantly tetravalent. Nevertheless, with this assumption an answer remained due to the question why no tetrachloride existed as for carbon and tin, for which the stannous salt was also written as the dimer $\text{Cl}_2\text{Sn=SnCl}_2$. Determinations of the molecular weight²¹ later showed that the dichlorides were monomeric, even at temperatures only just above their boiling points. The conclusions to which an excessive schematic application of the valence theory had led were thus in this case false; while for the trivalent metals, as far as the dimensions of the molecular weights of the halides were concerned, it had provided a correct prediction. Notwithstanding, the formulation it gave proved to be untenable. A metal-metal bond is not present in the halides of the trivalent metals. The impossibility of tetravalent aluminium follows unequivocally from the position of this metal in the Periodic System. For iron it does not appear to be excluded in the same manner, but the complete analogy in behaviour of AlCl_3 and FeCl_3 caused basically different formulations of the dimeric forms to appear contradictory. Thus one satisfied oneself with the assertion, which states nothing concerning the structure of the dimeric forms, that AlCl_3 and FeCl_3 associate, reassuring oneself still further by the fact that from about 700° upwards practically only the monomeric forms are present in equilibrium²².

A formulation of the dimeric trihalides which avoids a metal-metal bond is possible on the assumption of a halogen bridge. Formulae with one, two or all three halogen atoms as bridges are conceivable²³:

²⁰ W. MUTHMANN and W. NAGEL, *Ber.*, 1898, **31**, 2010.

²¹ SnCl_4 : H. BILTZ and V. MEYER, *Z. physik. Chem.*, 1888, **2**, 185; *Ber.*, 1888, **21**, 22.

²² That aluminium chloride possesses in ether the normal molecular weight AlCl_3 is not surprising, since it can form a complex with ether in which the central aluminium atom has either the co-ordination number 4 or 6.

²³ For the formulation of such dimeric compounds of the elements of group III, see B. EISTERT, *Z. physik. Chem.*, 1942, **B 52**, 202.

the RAMAN spectrum which, as for Al_2Cl_6 , is only compatible with the symmetry D_{2h} ³².

The methyl radical has thus the same function as a chlorine atom. This rôle does not appear surprising, inasmuch as it has almost the same molecular volume and the same molecular refraction as a chlorine atom, and on occasions can replace a chlorine atom isomorphously in organic compounds. Nevertheless, a characteristic difference with respect to chlorine exists, which assumes a considerable importance as soon as the *bonding functions of the electrons* are considered. A chlorine atom possesses, in addition to one unpaired valence electron, three lone pairs, whereas the methyl group on the contrary possesses none, since the corresponding three pairs are fixed in the C—H bonds. Consequently two methyl groups can supply only two electrons collectively for the bridge link, namely their unpaired valence electrons; whereas two chlorine atoms in the same circumstances, besides the corresponding two electrons, one from each, can also operate electrons from their lone pairs. In the old terminology of WERNER, one satisfied oneself with the assertion that the atoms providing the bridge link operated "subsidiary valencies" in the directions of the two aluminium atoms. Such manifestations of subsidiary valencies frequently consist in operating lone electron pairs. But the methyl group does not possess such a pair. A special investigation with regard to the activity of the electrons in polynuclear compounds with bridge bonds will consequently be required in order to obtain clarity concerning the nature of these subsidiary-valence manifestations. This will be undertaken later after the relationships with other polynuclear compounds containing halogen bridges have been discussed.

(ii) Mo_3Cl_6 , Mo_3Br_6 and Related Compounds

The trimeric molybdenum dichloride arises together with molybdenum tetrachloride by disproportionation of molybdenum trichloride³³, $2\text{MoCl}_3 \rightarrow \text{MoCl}_2 + \text{MoCl}_4$, or by the action of phosgene on powdered molybdenum³⁴ at about 600°. The dibromide is also obtainable by the former method. The chloride is yellow, the bromide yellowish red. Both are insoluble in water. The chloride dissolves in alcohol, in which it possesses a molecular weight corresponding to the formula Mo_3Cl_6 ³⁵. Both halides dissolve in alkalis giving a yellow coloration. In this a chemical reaction takes place, for acetic acid, and, in the case of the bromide, ammonium chloride

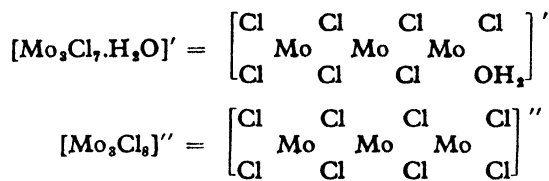
³² K. W. F. KOHLRAUSCH and J. WAGNER, *Z. physik. Chem.*, 1942, B 52, 185. Cf. also F. FEHÉR and W. KOLB, *Naturwissenschaften*, 1939, 27, 615. The older interpretation (N. R. DAVIDSON, J. A. C. HUGILL, H. A. SKINNER and L. E. SUTTON, *Trans. Faraday Soc.*, 1940, 36, 1212) is thereby to be regarded as superseded.

³³ C. W. BLOMSTRAND, *J. prakt. Chem.*, 1857, [i], 71, 449; 1859, [i], 77, 88; 1861, [i], 82, 433; *Ber.*, 1873, 6, 1464.

³⁴ K. LINDNER, *Ber.*, 1922, 55, 1458; K. LINDNER, E. HALLER and H. HELWIG, *Z. anorg. Chem.*, 1923, 130, 209.

³⁵ W. MUTHMANN and W. NAGEL, *Ber.*, 1898, 31, 2010.

one of hydrogen chloride are lost, is to be formulated $H[Mo_3Cl_7.H_2O].3H_2O$ ³⁹, or possibly more correctly $[H_3O][Mo_3Cl_7.H_2O].2H_2O$. The compound remaining after expulsion of H_2O and HCl is $Mo_3Cl_6.H_2O$, from which the water cannot be removed without complete decomposition. An established formula cannot be given for it. In contrast, for chloromolybdic acid from which it is formed, the trinuclear structure can be proved by means of a molecular-weight determination of its pyridine salt $[C_5H_5NH]Mo_3Cl_7.H_2O$ in nitrobenzene⁴⁰. The formulation of the complex it contains, it is true, remains hypothetical, like those of the anions of other chloro-acids which are obtained with hydrochloric acid from alkaline solutions of Mo_3Cl_6 , and are contained in the salts $K_2[Mo_3Cl_6].2H_2O$ and $K_2[Mo_3Cl_4Br_4].3H_2O$, for instance. The following formulae have been suggested for them⁴¹:



These formulations of the trinuclear anions are constructed according to the pattern of the dinuclear dimeric aluminium chloride.

The trinuclear anions of chlorotungstic acid $H[W_3Cl_7].4H_2O$ ⁴² and chlorotantalalic acid $H[Ta_3Cl_7].4H_2O$ ⁴³ are very probably constructed similarly to the chloromolybdic acids.

While in these trinuclear compounds bridges with two halogen atoms are to be accepted as very probable and the central atoms doubtless have the co-ordination number 4, in the complex dinuclear anions of trivalent tungsten and trivalent thallium bridges of three halogen atoms are present and the central atom has the co-ordination number 6, precisely as in the mononuclear halo-complexes AlF_6''' and $AlCl_6'''$ of trivalent aluminium. Here the spatial formula constructed, in the first place only formally, from two octahedra of chlorine atoms in contact by a triangular surface has been confirmed by X-ray investigations. This is true of the salts $K_3W_2Cl_9$ ⁴⁴ and $Cs_3Tl_2Cl_9$ ⁴⁵ (see Fig. 23):

³⁹ I. KOPPEL, *Z. anorg. Chem.*, 1912, **77**, 289.

⁴⁰ K. LINDNER, E. HALLER and H. HELWIG, *Z. anorg. Chem.*, 1923, **130**, 227.

⁴¹ H. J. EMELÉUS and J. S. ANDERSON, *Modern Aspects of Inorganic Chemistry*, p. 136 (Routledge, London, 1938).

⁴² J. B. HILL, *J. Am. Chem. Soc.*, 1916, **38**, 2383; K. LINDNER and A. KÖHLER, *Ber.*, 1922, **55**, 1464.

⁴³ W. H. CHAPIN, *J. Am. Chem. Soc.*, 1910, **32**, 324; K. LINDNER and H. FEIT, *Ber.*, 1922, **55**, 1464; 1465; *Z. anorg. Chem.*, 1924, **137**, 66. Cf. O. RUFF and F. THOMAS, *Ber.*, 1922, **55**, 1466; *Z. anorg. Chem.*, 1925, **148**, 1; 19.

⁴⁴ Preparation: O. O. COLLENBERG and K. SANDVED, *Z. anorg. Chem.*, 1923, **130**, 1 (also other salts). X-ray analysis: C. BROSSET, *Nature*, 1935, **135**, 874. $Cs_3W_2Cl_9$: *Arkiv Kemi Min. Geol.*, 1935, **12 A**, No. 4.

⁴⁵ H. M. POWELL and A. F. WELLS, *J. Chem. Soc.*, 1935, p. 1008; J. L. HOARD and L. GOLDSTEIN, *J. Chem. Phys.*, 1935, **3**, 199.

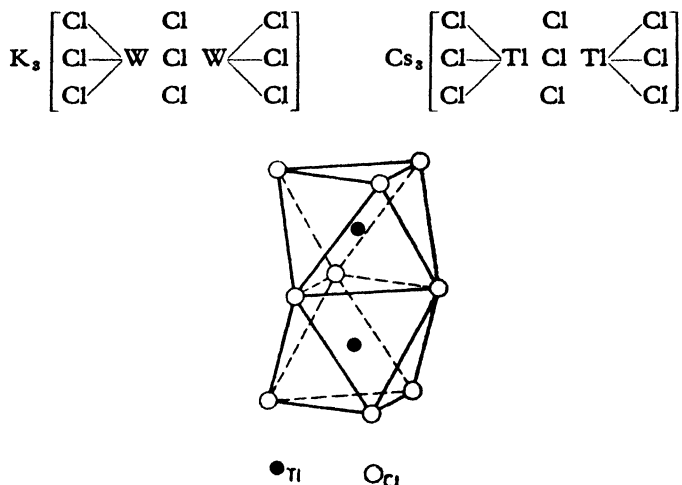


Fig. 23. Configuration of the $\text{Tl}_2\text{Cl}_9'''$ ion. The Tl atoms are not situated exactly in the middle of the chlorine octahedra, which contact one another at a surface. Consequently the Tl—Cl distances are not quite identical. The outer six chlorine atoms are situated at 2.5 Å, the three belonging to the mutual octahedral face at 2.8 Å from the central thallium atoms.

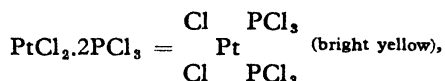
Other salts with analogous composition are known, *e.g.*, $\text{Cs}_3\text{Bi}_2\text{Cl}_9$ (= $3\text{CsCl} \cdot 2\text{BiCl}_3$)⁴⁶, yet according to the X-ray analysis of $\text{Cs}_3\text{As}_2\text{Cl}_9$ = $3\text{CsCl} \cdot 2\text{AsCl}_3$ ⁴⁷, which allows no polynuclear anion for this salt, it appears doubtful whether they are all constructed like the tungsten and thallium complexes. The AsCl_3 molecule, although slightly deformed, is to be recognized as such in the $\text{Cs}_3\text{As}_2\text{Cl}_9$ lattice. It forms a pyramid with the arsenic at the apex, the As—Cl distance being 2.25 Å and the $\text{Cl}-\text{As}-\text{Cl}$ angle $95^\circ 50'$, whereas in the free molecule the As—Cl distance bears the value 2.13 Å and the angle 107° (p. 126). In the lattice, the chlorine atoms of a second AsCl_3 molecule are certainly somewhat near (distance 2.75 Å). However, when making comparisons with salts possessing analogous empirical formulae, it must be remembered that the volatile AsCl_3 is not directly comparable with the involatile chlorides of trivalent metals. As long as no reliable X-ray analyses are available, all bridge formulae which theoretically may be constructed remain hypothetical and unproved. The same holds for the differently constructed halo-anions of antimony and bismuth which occur, for example, in the salts $\text{Rb}[\text{Sb}_2\text{Cl}_7] \cdot \text{H}_2\text{O}$ and $\text{Ni}[\text{Bi}_2\text{Cl}_7]_2 \cdot 12\text{H}_2\text{O}$. The polynuclear anions with halogen bridges are comparable with the polynuclear anions of pyro-acids, which contain oxygen bridges (p. 155), *e.g.*, RbSb_2Cl_7 and $\text{Na}_4\text{Sb}_2\text{O}_7$; cf. $\text{Cs}_3\text{Bi}_2\text{Cl}_9$ with $\text{Cu}_6\text{Bi}_4\text{S}_9$ (the mineral klaprotholite).

⁴⁶ $\text{Cs}_3\text{Bi}_2\text{I}_9$ has been suggested for the quantitative determination of caesium: N. A. TANANAEFF and E. P. HARMASCH, *Z. anal. Chem.*, 1932, 89, 256; cf., on the other hand, R. W. FELDMANN, *ibid.*, 1935, 102, 102.

⁴⁷ J. L. HOARD and L. GOLDSTEIN, *J. Chem. Phys.*, 1935, 3, 117.

(iii) Dinuclear Platinum and Palladium Compounds with Halogen Bridges

As has long been known, platinous chloride forms with phosphorus trichloride in addition to the mononuclear complex



also a molecular compound $\text{PtCl}_2 \cdot \text{PCl}_3$ (brownish red), which, according to WERNER⁴⁸, is dimeric and to be formulated with two chlorine bridges (see later). For other compounds of this type, a doubling of the simple formula has been proved by molecular-weight determinations, first for the compound with $\text{P}(\text{OC}_2\text{H}_5)_3$ (dark yellow) in place of PCl_3 , which arises smoothly from the phosphorus trichloride compound and alcohol⁴⁹, and then also for the compounds $[\text{PtCl}_2 \cdot \text{C}_2\text{H}_4]_2$ ⁵⁰ and $[\text{PdCl}_2 \cdot \text{PR}_3]_2$ ⁵¹. Instead of phosphorus trichloride, esters of orthophosphorous acid, ethylene and alkyl phosphines can thus be present, and arsines and thioethers in addition. Such compounds are known for both platinum and palladium⁵². The chlorine can be replaced wholly or partly by iodine, nitro groups or thiocyanate radicals. The compounds $[\text{PtCl}_2 \cdot \text{CO}]_2$ (golden yellow), prepared from the mononuclear compound $\text{PtCl}_2 \cdot 2\text{CO}$ (colourless) in a stream of carbon dioxide at 250°, and $[\text{PdCl}_2 \cdot \text{CO}]_2$ (yellowish red), prepared together with the mononuclear compound $\text{PdCl}_2 \cdot 2\text{CO}$ (yellow) from the red-brown PdCl_2 and carbon monoxide at 260°, also certainly belong here and are to be formulated as dimers, although a direct proof for this is lacking for these compounds.

A lone electron pair on the group containing the phosphorus, arsenic or sulphur is available for the bond to the central atom. In the case of ethylene, if the bond is to arise in the same way two electrons must be extracted from the double bond, and in the case of carbon monoxide from its shell of ten electrons. For carbon monoxide, such a contribution of an electron pair is met with in the metal carbonyls (Chapter VII, 7, (v)).

If it is assumed that the dinuclear complexes of divalent platinum and palladium are planar, as are the mononuclear, it follows that in them two squares make contact along a side, the written formula providing a direct portrayal of their structure. Accordingly stereoisomeric forms are to be expected, although such are in no case known so far, namely

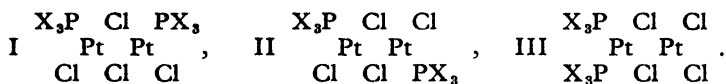
⁴⁸ According to R. F. WEINLAND, *Komplexverbindungen*, p. 418, footnote 1 (2nd Ed.).

⁴⁹ A. ROSENHEIM and W. LOEWENSTAMM, *Z. anorg. Chem.*, 1903, **37**, 394; A. ROSENHEIM and W. LEVY, *ibid.*, 1905, **43**, 35 (cryoscopic and ebullioscopic molecular-weight determinations in benzene).

⁵⁰ J. S. ANDERSON, *J. Chem. Soc.*, 1934, p. 971.

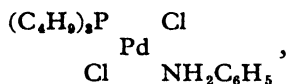
⁵¹ F. G. MANN and D. PURDIE, *J. Chem. Soc.*, 1936, p. 873.

⁵² $[\text{PdCl}_2 \cdot \text{PCl}_3]_2$, $[\text{PdCl}_2 \cdot \text{P}(\text{OR})_3]_2$: E. FINK, *Compt. rend.*, 1892, **115**, 76; *Ber.*, 1892, *Referate* **25**, 716. $[\text{PdCl}_2 \cdot \text{PR}_3]_2$, $[\text{PdCl}_2 \cdot \text{AsR}_3]_2$: F. G. MANN and D. PURDIE, *J. Chem. Soc.*, 1935, p. 1549.

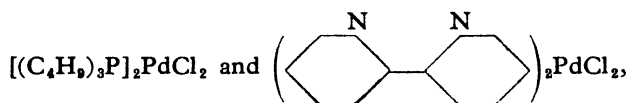


Finally the case would also be conceivable in which the compound PX_3 assumes the rôle of a bridge-forming substituent. If both bridges were formed in this manner, the isomerism would naturally not arise (see later).

Reactions permit no certain conclusions to be drawn concerning the distribution of the groups and the bridge atoms⁵³. The reaction of the complex tributylphosphine-palladium compound with aniline (or *para*-toluidine), which leads to two molecules of the mononuclear dichloro-anilino-tributylphosphine palladium

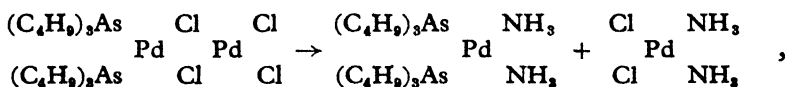


speaks for a *symmetrical* arrangement in the sense of formulae I and II. If nitro groups occupy the place of the chlorine, or if the cleavage is brought about by ammonia, the reaction proceeds similarly. In contrast, the same tributylphosphine-complex yields on cleavage by $\alpha:\alpha'$ -dipyridyl the mononuclear complexes dichloro-bis-tributylphosphine palladium and dichloro-bis- $\alpha:\alpha'$ -dipyridyl palladium,



which can only be explained by an unsymmetrical structure. Likewise the unsymmetrical formula may be concluded from cleavage by potassium oxalate and by sodium nitrite.

The relationships in the arsine-complexes of palladium are similar to those in its phosphine-complexes. It is noteworthy that the arsine-complexes undergo a cleavage by ammonia in the sense of the unsymmetrical formula

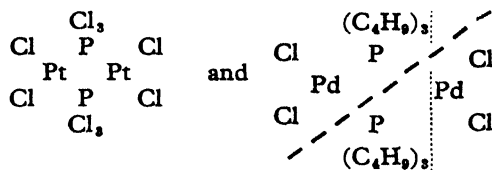


whereas the corresponding phosphine-complexes undergo a cleavage in the sense of the symmetrical formula.

In order to explain this strange behaviour, MANN and PURDIE assume a tautomeric equilibrium between the various possible structural and stereoisomeric forms, which would also make the indeterminate nature of the isomers demanded by theory comprehensible. Nevertheless, the easy change of position of the groups with the otherwise very firm bonding of the phosphorus and arsenic will here cause surprise. The hypothesis of an enigmatic tautomeric equilibrium can be avoided by the assumption that the

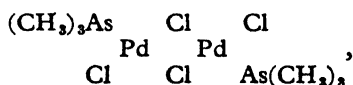
⁵³ F. G. MANN and D. PURDIE, *J. Chem. Soc.*, 1936, p. 873.

bridge is not formed by chlorine or other acid radicals, but by *neutral molecules*, e.g.,



According to whether the reagent divides the dinuclear complex symmetrically in the sense of the broken line, or unsymmetrically in the sense of the dotted line, either two molecules of the same mononuclear complex or two different mononuclear complexes arise. If this explanation is correct, then these compounds do not belong in the strict sense to the polynuclear halides with halogen bridges.

In one case so far examined, namely that of dibromo-bis-trimethylarsine- μ -dibromo dipalladium $[(\text{CH}_3)_3\text{AsPdBr}_2]_2$ and its isomeric chlorine compound, X-ray analysis has decided in favour of the formula with halogen bridges⁵⁴, in which the trimethylarsine groups are symmetrically placed to provide a centre of symmetry,



the angles on the palladium being almost 90° . It may not, of course, be taken as certain that all compounds of this kind have the same structure. In any case, chemical reactions are here again found to be inadequate for a determination of the structure.

Another class of dinuclear compounds with metals of the platinum group, in which chlorine bridges are to be assumed with certainty, are derived from *trivalent* platinum and palladium. The compounds of this class are non-electrolytes and arise by the careful oxidation of diammine platinumous salts or other corresponding complexes with nitrogen-containing compounds. If they were formulated as monomers, e.g., $\text{PtBr}_3 \cdot \text{NH}_3 \cdot \text{C}_2\text{H}_5\text{NH}_2$ ⁵⁵, $\text{PtCl}_3 \cdot \text{NH}_3 \cdot \text{C}_5\text{H}_5\text{N}$ ⁵⁶, $\text{PdCl}_3 \cdot 2\text{NH}_3$ (jet black)⁵⁶, the central atom would have the unusual co-ordination number 5. There need therefore be no doubt that they are dimeric.

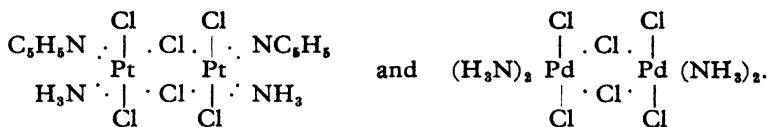
On this assumption, which however has not yet been proved by molecular-weight determinations, the following plausible formulation⁵⁷ with two chlorine bridges in which each central atom has the co-ordination number 6 is possible:

⁵⁴ F. G. MANN and A. F. WELLS, *J. Chem. Soc.*, 1938, p. 702; A. F. WELLS, *Proc. Roy. Soc.*, 1938, A 167, 169.

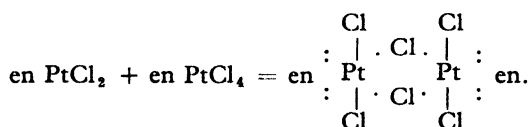
⁵⁵ S. M. JÖRGENSEN, *J. prakt. Chem.*, 1886, [ii], 33, 489.

⁵⁶ H. D. K. DREW, F. W. PINKARD, W. WARDLAW and E. G. COX, *J. Chem. Soc.*, 1932, p. 1013.

⁵⁷ F. G. MANN, *J. Chem. Soc.*, 1936, p. 873. The assumption of a Pt—Pt bond made by DREW, PINKARD, WARDLAW and COX (*loc. cit.*) need not be seriously discussed.



In these dinuclear compounds one may assume a joining up of two mononuclear compounds with trivalent atoms whose co-ordination number is 5 in the same way as in aluminium chloride and related compounds. Yet another explanation may however be substituted, according to which one central atom is divalent and the other tetravalent, that is, the trivalence is only apparent⁵⁸. It corresponds to the manner of formation of some of the compounds belonging here by direct union of one mononuclear complex with divalent and one with tetravalent metal⁵⁹, *e.g.*,



Since the deep colours which are a property of these dinuclear complexes are also otherwise met with in compounds containing the same metal in two states of valency with the possibility of an exchange of charge between the two metal atoms of different valency, of which Fe_3O_4 , Mn_3O_4 and Pb_3O_4 are examples, the assumption that di- and tetravalent atoms of the platinum metals exist side by side is for this reason not to be excluded.

Related to these complexes in structure are apparently⁶⁰ the compounds $[(\text{C}_2\text{H}_5\text{NH}_2)_4\text{PtCl}_3 \cdot \text{H}_2\text{O}]_2$, $[(\text{C}_2\text{H}_5\text{NH}_2)_4\text{PtCl}]_2\text{Cl}_4 \cdot 4\text{H}_2\text{O}$ and others.

(iv) The Kind of Bonding in Compounds with more than one Bridge

In a compound in which one, two or three atoms or groups of atoms form the bridge, except for a few cases the bond can be thought of in such a way, that each bridge atom supplies an otherwise not operated lone pair of electrons. Using the old notation of WERNER, it can be said that the bridge atom is linked by a principal valency to one central atom, whereas with respect to the second it manifests a subsidiary valency. However, as already mentioned, this conception has proved not to be applicable in two cases, namely in attempting to explain the dimeric form of aluminium trimethyl (p. 170) and the isomeric rhodo and erythro salts of chromium. As long as one speaks merely of a manifestation of subsidiary valence by the bridge atoms, without making the attempt to ascribe this to one particular lone pair of bonding electrons, no inherent contradiction of course results in the case of $\text{Al}_2(\text{CH}_3)_6$. But on attempting to ascribe the isomerism of the rhodo

⁵⁸ S. M. JÖRGENSEN, *J. prakt. Chem.*, 1886, [ii], **33**, 489.

⁵⁹ H. REIHLEN and E. FLOHR, *Ber.*, 1934, **67**, 2010, who however reject the formulation as a dinuclear compound.

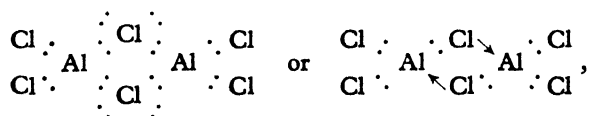
⁶⁰ H. REIHLEN and E. FLOHR, *Ber.*, 1934, **67**, 2010; H. D. K. DREW and H. J. TRESS, *J. Chem. Soc.*, **1935**, p. 1244.

and erythro salts to localized and distinguishable manifestations of subsidiary valence, a valence isomerism is arrived at which is otherwise never observed (p. 158). The example of dimeric aluminium trimethyl compels one to assume that the "manifestation of subsidiary valence" of the bridge methyl groups is to be sought in the interaction of four electrons and two bridge atoms in which, for the double bridge, each bridge atom and likewise each central atom contributes one electron. Thus, in contrast to what is otherwise assumed, the number of effective electrons between the bridge atoms and the central atoms is *not* eight, namely one from each central atom and bridge atom in principal-valence bonding (making a total of four electrons) plus two further lone electron pairs from the bridge atoms in subsidiary-valence bonding.

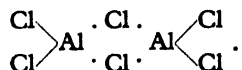
So far it has not been possible to provide any conception of where this interaction between the electrons and bridge atoms really arises. It is certain that for the solution of this problem the quantum theory must be drawn in. Presumably it would be best to develop the theory of this special type of link for the boron hydrides, for herein is provided the only possibility of making the bonding relationships understandable. Accordingly the sim-

plest boron hydride B_2H_6 is usually written $\begin{array}{c} H \\ \diagup \\ B \\ \diagdown \\ H \end{array} \cdot H \cdot \begin{array}{c} H \\ \diagdown \\ B \\ \diagup \\ H \end{array}$ (but see Chap-

ter VII, 6, (i)). Whatever the physical theory of such bridge links may be like, this much is certain, that normal electron-pair bonds are not being dealt with here. Consequently, even in those cases where the bridge links can be constructed by means of electron-pair bonds, one will also have to reckon with this other type of linking and, by way of example, instead of writing the formula for the Al_2Cl_6 molecule as



write it in a way which corresponds to the formulae for $Al_2(CH_3)_6$ and B_2H_6 , namely



The aluminium compounds are thereby to be thought of as constructed with a tetrahedral central atom, whereas the B_2H_6 molecule is apparently planar (cf. Chapter VII, 6, (i)). Whether and how far this type of bonding must be assumed to be general for bonding by bridge atoms remains for the time being, it must be admitted, an open question. But the fact that hydroxyl groups, as the bridge-forming ol groups, possess properties which are so very different from those normally found, is possibly to be attributed

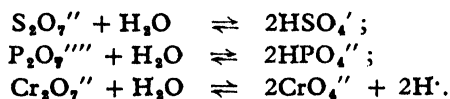
to such a special kind of bonding (cf. the difference with respect to a hydroxo group bound to only *one* central atom, p. 157).

Bridges such as those encountered here among molecules and complex ions of low molecular weight are met with again in infinite extension in crystal lattices. Examples which may be regarded as belonging here are the lattice of palladous chloride PdCl_2 (p. 118, Fig. 8), the lattice of cupric chloride CuCl_2 (Chapter VIII, 7, (ii)), the CdCl_2 chain in the lattice of the non-electrolyte $\text{Cl}_2\text{Cd}(\text{NH}_3)_2$ (pp. 122, 123), the anion in caesium cupric chloride CsCuCl_3 (p. 129) and the anions of a number of salts mentioned in conjunction with the last-named compound on page 129, and finally also the chain in silicon disulphide SiS_2 (Chapter VIII, 5, (iv)).

4. Heteropoly-acids

(i) General concerning Isopoly- and Heteropoly-acids

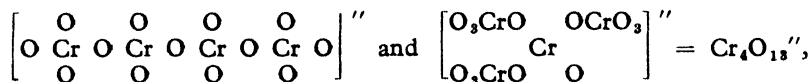
The linking of mononuclear complexes by bridge atoms is in principle no more limited than the linking of carbon atoms in organic chemistry by single, double or triple bonds. If the central atom has the co-ordination number 4 with a tetrahedral structure for the complex, then the analogy between the tetrahedral carbon atom operating four single bonds and a polynuclear compound held together by single bridges is still more extensive. The tetrahedra in the case of carbon are held together by electron pairs, in the case of the polynuclear compounds by oxygen atoms which in their turn are bound to two central atoms by two electron pairs. Accordingly it is to be expected that the same structural principles are possible for such polynuclear compounds as for carbon compounds, namely straight and branched chains. Thus, with a larger number of nuclei, there results, according to the branching, a structure which is more threadlike or more spherical. Otherwise than for carbon-carbon bonds, the oxygen bridges are in general much more easily broken, at least, as long as the polynuclear complexes are water soluble. Examples of this are the anions of the dinuclear pyro-acids, which in aqueous solution are either in equilibrium with the anion of the acid salt or of the neutral salt, *e.g.*,



Polynuclear acid anions which are not so extensively broken up by water constitute the *isopoly-acids*. The first stage in their formation occurs with the formation of the pyro-acids. Just as two identical acid anions can join themselves to one another, this is also possible when they are different.

In this case anions of *heteropoly-acids* arise. The co-ordination number of the central atoms in isopoly- and heteropoly-acids can be 3, 4 and 6. The co-ordination number 4 was originally chosen here as example only so as to be able to represent the linking up of acid radicals in better analogy to the principles of linking in carbon compounds. As in the carbon compounds, the possibilities of linking of a large number of acid anions appear to be unusually large. But only relatively few can be realized here, because the various forms usually enter into equilibria more or less rapidly. In consequence, on any particular occasion, only the stablest will be present in considerable concentration in aqueous solution, and only the least soluble salts separate out. Since equilibrium in aqueous solution does not bear a direct relationship to the solubility, the anion of the most insoluble salt does not always need to be at a considerable concentration in the equilibrium. For the equilibria of poly-acid anions in solution, a considerable dependence on the hydrogen-ion concentration may be expected from the experiments already carried out with the poly-acids, in particular the pyrochromates.

In the attempt to formulate the isopoly- and heteropoly-acids and so create a system, it seems obvious to begin with the crystalline compounds and, by means of one of the structural principles underlying the co-ordination theory, render their composition as determined by quantitative analysis intelligible. Since chemical structural proofs of the kind effected for carbon compounds are not possible here, such an attempt will cling to much that is hypothetical as long as no decision can be made between various conceivable possibilities by an analysis of the crystal structure. The isopoly-acids are not suited for the determination of a structural principle of this kind — if such a principle can be laid down as at all general — since it is equally impossible to decide upon a structure from the composition of an isopoly-acid anion as it is from the composition of a hydrocarbon. Thus for the tetrachromate ion $\text{Cr}_4\text{O}_{13}''$, for example, the structures



respectively derivable according to the principles of chainlike and centralized construction, have the same weight.

In contrast, for the heteropoly-acids it appears to be possible with a certain probability to infer a definite structural principle from the composition, provided that definite numerical ratios predominate between the various acid radicals and so permit the discovery of relations expressible by laws between the ratios found in the various heteropoly-acids. This is indeed the case, so that it is not surprising that views concerning the structures of poly-acid anions were first developed for the heteropoly-acids. ✓ A characteristic of the compositions of heteropoly-acids is the fact that to the acid radical of one acid is allotted a number of acid radicals of the other acid, the maximum being twelve. A centralized construction is thus

readily assumed for the anions, in which the central atom of the acid radical that is only singly represented forms the focus. The formulae constructed on this basis, for which in individual cases various other possibilities allow of discussion, will be discussed subsequently and related to the results of X-ray analysis. But a survey of the most important heteropoly-acids and a compilation of the elements from which they are derived will be given first.

(ii) Survey of the most important Heteropoly-acids

Heteropoly-acids can be formed by several elements whose oxides possess acidic character. This tendency is most marked for elements of subgroups Va and VIa of the Periodic System that are also able to form isopoly-acids, especially molybdenum, tungsten and vanadium. Several combining weights of their oxides enter into combination with one combining weight of the oxides of boron, silicon and phosphorus, which likewise form isopoly-acids, as well as of arsenic. These acids, borotungstic, silicotungstic, phosphomolybdic, etc., are however only one, though an especially important, group of heteropoly-acids. The whole class of compounds was first studied by means of them. Ammonium phosphomolybdate $(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3$ was discovered in 1826 by BERZELIUS and introduced into analytical chemistry in 1848 by SVANBERG and STRUVE⁶¹, though the analytical composition of heteropoly-acids and their salts has been more precisely determined only since the discovery of silicotungstic acid and its salts by MARIGNAC in 1862⁶².

In the course of time, the number of compounds to be reckoned as belonging to the heteropoly-acids multiplied in an extraordinarily rapid manner, especially through the investigations of WOLCOTT GIBBS, C. FRIEDHEIM, A. ROSENHEIM, A. MIOLATI, F. KEHRMANN, H. COPAUX and W. PRANDTL, so that today not even a moderately complete compilation of them exists⁶³. Such will also not be provided in the following survey, which presents only a very modest arbitrary selection showing how varied this whole class of compounds is. Only the empirical compositions from the oxides are given here⁶⁴:

phosphomolybdic acid (yellow)	$\text{P}_2\text{O}_5 \cdot 24\text{MoO}_3 \cdot 63\text{H}_2\text{O}$
potassium salt (yellow)	$\text{P}_2\text{O}_5 \cdot 24\text{MoO}_3 \cdot 3\text{K}_2\text{O}$
potassium salt of another phosphomolybdic acid (yellow).	$\text{P}_2\text{O}_5 \cdot 20\text{MoO}_3 \cdot 3\text{K}_2\text{O} \cdot 3\text{H}_2\text{O}$

⁶¹ L. SVANBERG and H. STRUVE, *J. prakt. Chem.*, 1848, [i], 44, 257; 291; H. STRUVE, *ibid.*, 1851, [i], 54, 288.

⁶² C. MARIGNAC, *Compt. rend.*, 1862, 55, 888; *Liebigs Ann. Chem.*, 1863, 125, 362.

⁶³ Such compilations have been given many years ago by H. COPAUX, *Compt. rend.*, 1909, 148, 633; *Ann. chim. phys.*, 1909, [viii], 17, 217. Also R. HABERLE, *Inaug. Diss.*, Berlin, 1911 (p. 8). The collective (and also historical) presentation of A. ROSENHEIM and J. JAENICKE, *Z. anorg. Chem.*, 1917, 100, 304, deals chiefly with the boro-, silico- and phosphomolybdic and -tungstic acids.

⁶⁴ Further examples are given in R. F. WEINLAND's *Einführung in die Chemie der Komplexverbindungen*, p. 377 ff (Stuttgart, 1919); 2nd Ed., p. 433 ff (1924).

phosphotungstic acid (white)	$P_2O_5.24WO_3.63H_2O$
silicomolybdic acid (white)	$SiO_2.12MoO_3.32H_2O$
silicotungstic acid (white)	$SiO_2.12WO_3.32H_2O$
borotungstic acid (white)	$B_2O_3.24WO_3.65H_2O$
periodotungstic acid	$I_2O_7.12WO_3.11H_2O$
salts of vanadiselenious acid (yellow)	$2SeO_2.V_2O_5.K_2O.H_2O$
salts of vanadiselenious acid (orange)	$10SeO_2.7V_2O_5.2Na_2O.13H_2O$
salts of vanadiselenious acid (orange)	$26SeO_2.10V_2O_5.5K_2O.43H_2O$
potassium salt of chromimolybdic acid (rose red)	$Cr_2O_3.12MoO_3.3K_2O.20H_2O$

Al^{III} , Fe^{III} , Mn^{III} , Co^{III} and Rh^{III} can also take the place of Cr^{III} in heteropoly-acids⁶⁵.

In addition, complexes of telluric acid and sulphuric acid with molybdic acid, and of iodic acid and vanadic acid with phosphoric and arsenic acids are known. Molybdic acid can also unite with hypophosphorous, arsenious and antimonious acids, among others.

On occasions, heteropoly-acids formed from three acids have also been observed, *e.g.*, the ammonium salt of vanadic acid-silicic acid-tungstic acid, $V_2O_5.SiO_2.9WO_3.3(NH_4)_2O.24H_2O$.

(iii) Formation and Properties of the Heteropoly-acids⁶⁶

Because of the great variety of heteropoly-acids and their salts it is impossible to give a general characterization of them. There will therefore be a limitation here essentially to the best-investigated poly-acids of molybdenum and tungsten with boric, silicic, phosphoric and arsenic acids⁶⁷.

Preparation. — The silicotungstic and borotungstic acids have been chosen as examples of the manner of formation.

Freshly precipitated silica dissolves in hot aqueous solutions of acid alkali tungstates obtained by treating tungstates, which react alkaline in consequence of hydrolysis, with hydrochloric acid until they give a neutral reaction. The solution thereby becomes weakly alkaline, and is therefore acidified with a little hydrochloric acid. In this manner, well-crystallized salts are obtained⁶⁸. The free acid is best obtained by shaking a concentrated solution of the sodium salt with ether and adding concentrated hydrochloric

⁶⁵ H. STRUVE, *J. prakt. Chem.*, 1854, [i], **61**, 449; A. ROSENHEIM and H. SCHWER, *Z. anorg. Chem.*, 1914, **89**, 224.

⁶⁶ Cf. with respect to this and the following sections K. F. JAHR, *Ueber Eigenschaften, Bildungsweise und Struktur der Heteropolysäuren*, *Naturwissenschaften*, 1941, **29**, 505.

⁶⁷ Compilation: A. ROSENHEIM and J. JAENICKE, *Z. anorg. Chem.*, 1917, **100**, 304. The theoretical views to be found therein are now for the most part superseded (see later).

⁶⁸ C. MARIGNAC, *Liebigs Ann. Chem.*, 1863, **125**, 362; *Ann. chim. phys.*, 1864 [iv], **3**, 5.

acid⁶⁹, or alternatively by decomposing the barium salt with sulphuric acid, or the mercurous salt with hydrochloric acid⁷⁰.

The potassium salt⁷¹ has the composition $\text{SiO}_2 \cdot 12\text{WO}_3 \cdot 4\text{K}_2\text{O} \cdot 18\text{H}_2\text{O}$. The free silicotungstic acid $\text{SiO}_2 \cdot 12\text{WO}_3 \cdot 32\text{H}_2\text{O}$ is readily converted to $\text{SiO}_2 \cdot 12\text{WO}_3 \cdot 26\text{H}_2\text{O}$.

If one starts with an alkaline solution of $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ plus sodium silicate and then acidifies with acetic acid⁷², one obtains in addition yet another acid, which for differentiation has been named tungstosilicic acid.

The potassium salt has the composition⁷³ $\text{SiO}_2 \cdot 12\text{WO}_3 \cdot 4\text{K}_2\text{O} \cdot 9\text{H}_2\text{O}$, and the free tungstosilicic acid $\text{SiO}_2 \cdot 12\text{WO}_3 \cdot 24\text{H}_2\text{O}$. It cannot be obtained from silicotungstic acid by the removal of water, and only by heating under pressure with water to 150° is it converted into the latter acid (for further, see later).

If an ammonium tungstate solution is boiled with freshly precipitated silicic acid and the ammonium salt formed subsequently treated with ammonia, the salt which results is of a silicotungstic acid containing only ten WO_3 to one SiO_2 . In weakly alkaline solution, therefore, fewer than twelve WO_3 remain bound with SiO_2 .

Borotungstic acid is very easily formed by evaporating sodium tungstate Na_2WO_4 with boric acid⁷⁴. Here also two different acids are obtained:

Borotungstic acid of the composition $\text{B}_2\text{O}_3 \cdot 24\text{WO}_3 \cdot 65\text{H}_2\text{O}$, which can be dehydrated to $\text{B}_2\text{O}_3 \cdot 24\text{WO}_3 \cdot 28\text{H}_2\text{O}$;

Tungstoboric acid of the composition $\text{B}_2\text{O}_3 \cdot 24\text{WO}_3 \cdot 51\text{H}_2\text{O}$.

Borotungstic and tungstoboric acids cannot be interconverted by repeated treatment with water or on concentration by evaporation. Borotungstic acids with less than 12 WO_3 to one boron atom are not so far known, either in the free state or as salts.

Stability. — The heteropoly-acids are stable only in acid or neutral solution. In alkaline solution they undergo hydrolysis. In this it is possible under certain circumstances to note various intermediate stages which contain less than twelve WO_3 or MoO_3 respectively per silicon or phosphorus atom, of which an example is given above. A stepwise degradation of this sort can be followed even better with phosphotungstic acid, which leads to salts of acids with P : WO_3 ratios 1 : 11, 2 : 21 and 2 : 17⁷⁵. The acid which is otherwise very easily obtained from sodium tungstate

⁶⁹ E. DRECHSEL, *Ber.*, 1887, **20**, 1452.

⁷⁰ C. MARIGNAC, *Ann. chim. phys.*, 1864, [iv], **3**, 11. Cf. also A. ROSENHEIM and J. JAENICKE, *Z. anorg. Chem.*, 1917, **101**, 223.

⁷¹ C. MARIGNAC, *Ann. chim. phys.*, 1864, [iv], **3**, 20; A. ROSENHEIM and J. JAENICKE *Z. anorg. Chem.*, 1917, **101**, 242.

⁷² H. COPAUX, *Bull. soc. chim. France*, 1908, [iv], **3**, 101.

⁷³ C. MARIGNAC, *Ann. chim. phys.*, 1864, [iv], **3**, 48; H. COPAUX, *loc. cit.*; A. ROSENHEIM and J. JAENICKE, *op. cit.*, p. 243.

⁷⁴ D. KLEIN, *Bull. soc. chim. France*, 1884, [ii], **35**, 12; H. COPAUX, *Ann. chim. phys.*, 1909, [viii], **17**, 217.

⁷⁵ The investigations of F. KEHRMANN and of other investigators concerning these acids are cited by A. ROSENHEIM and J. JAENICKE, *Z. anorg. Chem.*, 1917, **101**, 251; 257 ff.

and a large excess of syrupy phosphoric acid, namely that with the ratio 1 : 9 ($P_2O_5 \cdot 18WO_3 \cdot 42H_2O$), is only to be detected in small quantities in the degradation of acids containing more WO_3 .⁷⁵

Hydrolysis in alkaline solution renders the determination of the basicity of the acids, of which more will be said later, very much more difficult.

In stability the heteropoly-acids of molybdenum and tungsten with amphoteric oxides of trivalent metals, like those with telluric and iodic acids, are very different from the phospho-, silico- and borotungstic and -molybdic acids, since the free acids are not capable of existence. Only salts of the following corresponding types are known: $R_3H_6[M^{III}(MoO_4)_6] \cdot 7H_2O$ (a few salts of the type $R_4H_5[M^{III}(MoO_4)_6]$ have also been prepared); $R_4H_5[Fe^{III}(WO_4)_6] \cdot xH_2O$; $R_6[Te(MoO_4)_6] \cdot xH_2O$; $R_5[I(MoO_4)_6] \cdot xH_2O$. The justification for the manner of writing the complexes will be seen later.

Solubility. — The free heteropoly-acids are extraordinarily easily soluble in water⁷⁶, even in a fifth to a seventh of their weight, and likewise in alcohol. On warming with ether, viscous oils are formed which can be somewhat diluted with ether, but which with more ether yield two phases. Much water splits up the oil into an aqueous solution of the acid and ether. The oils are certainly not ordinary solutions of the acids in ether, but possibly loose oxonium compounds.

Crystallography. — Good crystals can be obtained of almost all the salts as well as of the free acids. The free acids containing twelve MoO_3 or WO_3 groups exist in two differently hydrated forms. All the water-rich hydrates form tetragonal bipyramids which are nearly regular octahedra, whereas those poorer in water crystallize in rhombohedra. All the water-rich hydrates are isomorphous with one another and form continuous series of mixed crystals, as do also those with less water among themselves⁷⁷. The acids containing nine MoO_3 or WO_3 groups, $P(As)_2O_5 \cdot 18Mo(W)O_3 \cdot 42H_2O$, are also isomorphous. Likewise among the salts numerous isomorphous series are found. The potassium salts of the acids with twelve groups exhibit enantiomorphism. Frequently isomorphism also exists between free acids and their salts, for example, between borotungstic acid and ammonium borotungstate⁷⁸, silicotungstic acid and lithium silicotungstate⁷⁹, and also phosphotungstic acid and sodium phosphotungstate⁸⁰. Whereas the isomorphism between the free acids, their ammonium salts and their alkali salts is not surprising, since the hydroxonium ion H_3O^+ is able to take up the position of NH_4^+ , the substitution of two monovalent ions, e.g., two sodium ions, by one divalent ion, and the isomorphism of the free acids with their

⁷⁶ H. COPAUX, *Ann. chim. phys.*, 1906, [viii], 7, 127.

⁷⁷ D. KLEIN, *Bull. soc. franç. minéral.*, 1882, 5, 263; A. ROSENHEIM and J. JAENICKE, *Z. anorg. Chem.*, 1912, 77, 250. Isomorphous relationships by virtue of X-ray analyses: O. KRAUS, *Z. Krist.*, 1935, 91, 402. For further references, see p. 187, footnote 98.

⁷⁸ H. COPAUX, *Bull. soc. chim. France*, 1908, [iv], 3, 101.

⁷⁹ H. COPAUX, *Bull. soc. franç. minéral.*, 1906, 29, 77.

⁸⁰ M. SOBOLEW, *Z. anorg. Chem.*, 1896, 12, 16.

alkaline-earth salts is remarkable. The isomorphism between barium silicomolybdate and free silicotungstic acid is to be regarded in the same light. Here, at a preliminary glance, the different water content is surprising⁸¹: $\text{BaO} \cdot \text{SiO}_2 \cdot 12\text{MoO}_3 \cdot 24\text{H}_2\text{O}$, isomorphous with $\text{SiO}_2 \cdot 12\text{MoO}_3 \cdot 28\text{H}_2\text{O}$, in which for the $28\text{H}_2\text{O}$ may be written $[\text{H}_3\text{O}]_2[\text{O} \cdot \text{H}_2\text{O}] \cdot 24\text{H}_2\text{O}$.

Much more remarkable is the isomorphism between ammonium borotungstate $5(\text{NH}_4)_2\text{O} \cdot \text{B}_2\text{O}_3 \cdot 24\text{WO}_3 \cdot 52\text{H}_2\text{O}$ and ammonium metatungstate $(\text{NH}_4)_2\text{O} \cdot 24\text{WO}_3 \cdot 48\text{H}_2\text{O}$ ⁸². From this it follows that the so-called metatungstates are, according to their structure, to be placed along with the heteropoly-acids, even though they contain no hetero atom.

Generally speaking, by reason of the crystallographic relationships it may be stated that the crystal structure depends essentially on the number of molybdic or tungstic acid groups, but can be modified in detail by the number of water molecules, while the nature of the cations⁸³ plays a subordinate rôle. The recognition of this is important, because, in consequence, the results of the X-ray analysis of *one* compound may be transferred without appreciable restraint to compounds isomorphous with it.

Basicity. — The determination of the basicity of heteropoly-acids, as already mentioned, causes difficulties on account of the hydrolysis of the complexes that sets in in alkaline solution, even though the heteropoly-acids as such are strong acids⁸⁴. In most of their salts, phosphotungstic acid is tribasic, silicotungstic acid is tetrabasic, and borotungstic acid is pentabasic, the molybdates corresponding. Generally the basicity principally observed in the complex can be expressed by the formula $\text{H}_{8-n}\text{R}^n\text{O}_4$, in which n signifies the valency of the central atom when the "parent acid" is written with the co-ordination number 4. For phosphorus and silicon, H_3PO_4 and H_4SiO_4 are familiar, the latter at least from its salts, but for boron the like does not of course occur, not even as salts. In addition to this basicity which appears as predominating, there appeared at one time to be yet another and higher one, which usually exceeded it by 4. But with the passage of time, none of the proofs brought forward for such a high basicity have proved themselves to be sound, and the doubts which various investigators⁸⁵ have expressed against the high basicity have been justified. But this higher (according to COPAUX⁸⁶ secondary) basicity, as distinct from the usual (according to COPAUX⁸⁶ primary) basicity, with which it was even frequently spoken of in one and the same breath⁸⁷, played a very important rôle for several decades, and, as we now know, led to

⁸¹ A. ROSENHEIM and J. JAENICKE, *Z. anorg. Chem.*, 1917, **100**, 313.

⁸² H. COPAUX, *Ann. chim. phys.*, 1909, [viii], **17**, 256.

⁸³ Dependence of the lattice type on the cation: O. KRAUS, *Z. Krist.*, 1936, **94**, 256 = *Fortschr. Min. Krist. Petr.*, 1937, **21**, 63.

⁸⁴ H. COPAUX, *Bull. soc. chim. France*, 1913, [iv], **13**, 324; E. PÉCHARD, *Ann. chim. phys.*, 1891, [vi], **22**, 198.

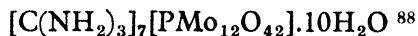
⁸⁵ See, for example, F. KEHRMANN, *Z. anorg. Chem.*, 1904, **39**, 98.

⁸⁶ H. COPAUX, *Compt. rend.*, 1913, **156**, 71; *Bull. soc. chim. France*, 1913, [iv], **13**, 324.

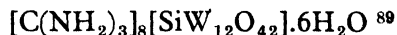
⁸⁷ A. ROSENHEIM and J. JAENICKE, *Z. anorg. Chem.*, 1917, **100**, 345.

error. Consequently the apparent evidence cannot be passed over completely in the discussion of the formulation of the heteropoly-acids.

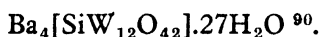
That with the greatest weight appeared to be the preparation of the guanidinium salts, especially those of the heptabasic phosphomolybdic acid



and of the octabasic silicotungstic acid



by ROSENHEIM and his school, who were also able to confirm in part the analytical findings of earlier investigators for other salts which also indicated such high basicities, for example, the barium salt of tungstosilicic acid,



In other cases, certainly, he was able to prove that the salts believed to have been derived from acids with the limit of twelve WO_3 or MoO_3 groups and such a high basicity were in reality salts of acids poorer in tungstic and molybdic acids. For example, the salt formulated by MARIGNAC⁹¹ as $\text{K}_8[\text{SiW}_{12}\text{O}_{42}]\cdot 14\text{H}_2\text{O}$ proved to be $7\text{K}_2\text{O}\cdot 2\text{SiO}_2\cdot 20\text{WO}_3\cdot 11\text{H}_2\text{O}$ or $\text{K}_7\text{H}[\text{SiW}_{10}\text{O}_{36}]\cdot 11\text{H}_2\text{O}$ ⁹², being thus derived from a 10-tungstic acid. A recent careful check of ROSENHEIM's work by P. SOUCHAY⁹³ has shown that ROSENHEIM himself, in all his salts which he believed to be derived from an acid of high basicity and the limiting number of twelve WO_3 or MoO_3 groups, had become a victim of the same mistake as that of which he showed MARIGNAC to be guilty in individual cases. A part of the tungstic or molybdic acid is hydrolyzed off by the guanidinium carbonate which is utilized in the preparation of the salts and has a basic reaction, so that in reality salts of the acids with twelve groups are not subjected to analysis⁹⁴.

Even if every piece of evidence for the high basicity of the heteropoly-acids has not yet been individually demonstrated with equal certainty to be inapplicable, a conclusiveness will no longer be ascribed to any of them, for in every case the possibility has to be considered that neither the limiting acid nor its salts has been investigated, but an acid with less than twelve WO_3 or MoO_3 groups. Furthermore, not only the purely analytical but also

⁸⁸ A. ROSENHEIM and J. JAENICKE, *Z. anorg. Chem.*, 1917, **101**, 244.

⁸⁹ R. HÄBERLE, *Diss.*, Berlin, 1911 (p. 36); A. ROSENHEIM and J. JAENICKE, *Z. anorg. Chem.*, 1917, **100**, 344.

⁹⁰ A. ROSENHEIM and J. JAENICKE, *Z. anorg. Chem.*, 1917, **101**, 244.

⁹¹ C. MARIGNAC, *Ann. chim. phys.*, 1864, [iv], **3**, 19.

⁹² F. KEHRMANN, *Z. anorg. Chem.*, 1904, **39**, 104; confirmed by A. ROSENHEIM and J. JAENICKE, *Z. anorg. Chem.*, 1917, **101**, 246. R. F. WEINLAND in his *Einführung in die Chemie der Komplexverbindungen* (1919) has not considered this, since on p. 380 he still formulates the salt $\text{K}_8[\text{Si}(\text{W}_7\text{O}_7)_6]\cdot 14\text{H}_2\text{O}$. It appears completely within the bounds of possibility that similar corrections must also be made with respect to the investigations of MARIGNAC cited in footnote 91.

⁹³ P. SOUCHAY, *Bull. soc. chim. France*, 1942, [v], **9**, 289.

⁹⁴ Other salts, which MARIGNAC considered to be salts of heteropoly-acids of high basicity, e.g., $\text{Hg}_8[\text{SiW}_{12}\text{O}_{42}]$, have also since been proved by SOUCHAY to be wrongly formulated for the same reason.

the physicochemical proofs, which MIOLATI⁹⁵ believed he had adduced by the determination of neutrality curves and conductivities, are linked to the same sources of error, namely the possibility of a part of the acid radical becoming hydrolyzed off during the experiment. The results may well be right in themselves: nevertheless, they are not to be referred to the limiting acids but to other acids.

For the acids which are not limiting acids, high basicities will still have to be reckoned with on account of the results of both ROSENHEIM and SOUCHAY which agree on this point.

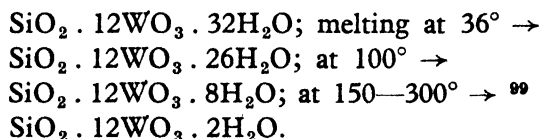
The formulation of the heteropoly-acids as acids with high basicities was possible because the salts, like the acids, usually contain many water molecules, so that the hydrogen can be relegated to the cation as desired and the oxygen to the anion. At the same time, the fact that this was not always applicable spoke against the high basicity, since in many cases the necessary water was either wholly or partly lacking.

The best-known example is ammonium phosphomolybdate, which serves for the quantitative estimation of phosphoric acid. Precipitated from a nitric acid solution it has the composition⁹⁶



thus just allowing itself, if the NO_3 groups are included in the anion (!), to be written as an acid salt of a heptabasic acid. Dried at 180° to constant weight it loses HNO_3 and H_2O and is converted to the neutral salt $(\text{NH}_4)_3\text{PMo}_{12}\text{O}_{40}$, which can only be derived from a tribasic phosphomolybdic acid. Other examples are $(\text{NH}_4)_3\text{AsW}_{12}\text{O}_{40}$ and the acid salts $\text{Ti}_3\text{HSiW}_{12}\text{O}_{40}$ and $(\text{NH}_4)_3\text{H}[\text{SiMo}_{12}\text{O}_{40}]$, which are related to the tetrabasic acids. The precipitates which phosphotungstic acid and silicotungstic acid form with numerous organic bases are also anhydrous⁹⁷.

Even free acids can be dehydrated beyond the water content corresponding to their supposed maximum valency without fundamentally altering them, in which case the water is given up in clearly distinguishable steps⁹⁸. For silicotungstic acid these are the following:



Tungstosilicic acid likewise loses its water except for two molecules in two clearly distinguishable stages:

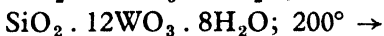
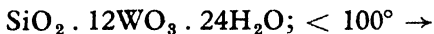
⁹⁵ A. MIOLATI, *Gazz. chim. ital.*, 1903, **33**, II, 335; A. MIOLATI and R. PIZZIGHELLI, *J. prakt. Chem.*, 1908, [ii], **77**, 434.

⁹⁶ R. FINKENER, *Ber.*, 1878, **11**, 1640; E. HINTZ, *Z. anal. Chem.*, 1882, **21**, 566; cf. F. HUNDESHAGEN, *ibid.*, 1889, **28**, 144.

⁹⁷ E. KAHANE and M. KAHANE, *Bull. soc. chim. France*, 1931, [iv], **49**, 557.

⁹⁸ Compilation of all certainly known hydrates: O. KRAUS, *Naturwissenschaften*, 1937, **25**, 250.

⁹⁹ A. G. SCROGGIE and G. L. CLARK, *Proc. Nat. Acad. Sci., U.S.*, 1929, **15**, 1; A. ROSENHEIM, *Z. anorg. Chem.*, 1934, **220**, 73.



The two last molecules of water are firmly retained, even at 300° . During this dehydration, the acid preserves its individuality, for when dissolved afresh in water it comes out again with $24\text{H}_2\text{O}$ and remains distinguishable from silicotungstic acid. But if the aqueous solution or that of its potassium salt is heated under pressure to 150° , it is transformed into silicotungstic acid¹⁰⁰.

5. Formulation of the Heteropoly-acids

The following possibilities permit of discussion solely on the basis of the analytically determined composition, and without reference to the chemical properties.

The existence of a limiting series with twelve MoO_3 or WO_3 groups respectively indicates that a chainlike linking up of the structural units is very improbable. It need not therefore be discussed further here¹⁰¹.

With a centralized construction, the following arrangements occur for the limiting series if it is desired to distribute the acid radicals evenly about the central atom, since the number 12 is divisible by 2, 3 and 4¹⁰²:

- (i) co-ordination number of central atom 12, twelve oxygen atoms effecting the bonding to the central atom, that is, the anion¹⁰³ becomes
- $$\text{X}^{n+} + 12\text{WO}_3 + 12\text{O}'' = \text{X}^{n+} + 12\text{WO}_4'' = [\text{X}(\text{WO}_4)_{12}]^{(24-n)-};$$
- (ii) co-ordination number of central atom 6, six oxygen atoms effecting the bonding to the central atom, that is, the ion becomes
- $$\text{X}^{n+} + (6 \times 2)\text{WO}_3 + 6\text{O}'' = \text{X}^{n+} + 6\text{W}_2\text{O}_7'' = [\text{X}(\text{W}_2\text{O}_7)_6]^{(12-n)-};$$
- (iii) co-ordination number of central atom 4, four oxygen atoms effecting the bonding to the central atom, that is, the ion becomes
- $$\text{X}^{n+} + (4 \times 3)\text{WO}_3 + 4\text{O}'' = \text{X}^{n+} + 4\text{W}_3\text{O}_{10}'' = [\text{X}(\text{W}_3\text{O}_{10})_4]^{(8-n)-};$$
- (iv) co-ordination number of central atom 3, three oxygen atoms effecting the bonding to the central atom, that is, the ion becomes
- $$\text{X}^{n+} + (3 \times 4)\text{WO}_3 + 3\text{O}'' = \text{X}^{n+} + 3\text{W}_4\text{O}_{13}'' = [\text{X}(\text{W}_4\text{O}_{13})_3]^{(6-n)-}.$$

The co-ordination number 12, which otherwise occurs only with the closest packing of spheres in metal lattices, may be dropped from the outset¹⁰⁴,

¹⁰⁰ H. COPAUX, *Bull. soc. chim. France*, 1908, [iv], 3, 107.

¹⁰¹ Concerning the rôle the chain formulae have played in the historical development of heteropoly-acids, see A. ROSENHEIM and J. JAENICKE, *Z. anorg. Chem.*, 1917, 100, 326.

¹⁰² These possibilities are briefly indicated by A. ROSENHEIM and J. JAENICKE, *op. cit.*, pp. 332—333.

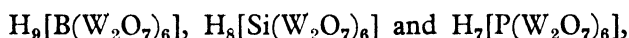
¹⁰³ For the sake of simplicity, in reckoning the charge of the anion the procedure has been to insert the WO_3 or MoO_3 respectively as the neutral part, the central atom as positive and the oxygen as negative ion.

¹⁰⁴ P. PFEIFFER (*Z. anorg. Chem.*, 1918, 105, 30) has attempted to surmount this difficulty by assuming that six oxygen atoms are arranged octahedrally in the first sphere and twelve WO_3 molecules cubo-octahedrally (at the centres of the edges of a cube).

especially in view of the relative smallness of the central atom. In addition, the co-ordination number 3 is very improbable, especially for Si, P and As, since isolated SiO_3'' , PO_3' and AsO_3' ions do not occur in the lattice.

There remains, therefore, the option of assuming the co-ordination number 4 or 6 for the central atom. For the co-ordination number 6 it may be mentioned that silicon and phosphorus, at least, possess it in the fluo-silicates and fluophosphates, and that although it does not occur in the anions of the oxy-acids of silicon and phosphorus, it does in the oxy-acid anions of H_6TeO_6 and H_5IO_6 . The latter likewise form heteropoly-acids, though less stable ones. Against the co-ordination number 6 may be mentioned the fact that it appears improbable, at least in the case of boron, on account of the smallness of its atom, which, even with fluorine in the BF_4' ion, is able to arrange only four atoms about itself. On the other hand, from the outset it is not possible to bring valid objections against the co-ordination number 4, which is the usual co-ordination number in the anions of oxy-acids.

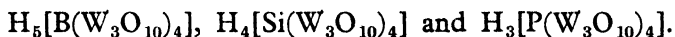
Based on the co-ordination number 6, the following formulae result for the most important types of limiting acids, namely



which are derived from the hypothetical parent acids H_9BO_6 , H_8SiO_6 and H_7PO_6 by replacing the oxygen with the pyro groups W_2O_7 or Mo_2O_7 .

This hypothesis was advanced by A. MIOLATI¹⁰⁵. Later A. ROSENHEIM attempted to support it, in that he believed he had obtained salts corresponding to the high-basicity formulae of the acids. It is therefore known as the MIOLATI-ROSENHEIM theory. H. COPAUX also made use of this formulation (see previously).

Based on the co-ordination number 4, the formulation of the corresponding types of limiting acids becomes:

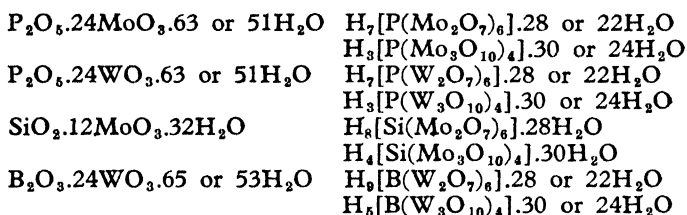


It is immediately seen that the basicity of these acids corresponds to the basicity which is usually observed for the heteropoly-acids. The basicity which is higher by 4 corresponds to the occasionally observed maximum basicity of the acids formulated with the co-ordination number 6 for the central atom, as ROSENHEIM proved for a few acids containing ten WO_3

¹⁰⁵ A. MIOLATI and R. PIZZIGHELLI, *J. prakt. Chem.*, 1908, [ii], 77, 417. Actually A. WERNER (*Neuere Anschauungen auf dem Gebiete der anorganischen Chemie*, p. 289, 2nd Ed., 1909) made use of very similar formulae, but inconsistently retained in them the distinction between principal- and subsidiary-valence bonding in order to explain the isomerism of silicotungstic acid and tungstosilicic acid sterically as *cis-trans* isomerism on an octahedron. For their salts he had then to assume bonding of the cations to particular acid radicals, possessing edgewise and axial configurations respectively, in order to be able to give the same explanation of the isomerism. In this respect, see the explanations of A. ROSENHEIM and J. JAENICKE, *Z. anorg. Chem.*, 1917, 100, 331—337. Today this sort of explanation of isomerism appears to us as completely erroneous.

or MoO_3 groups¹⁰⁶. The formulae with the co-ordination number 6 are not compatible with the existence of anhydrous salts and acids containing less water: those with the co-ordination number 4 are only inapplicable for the acids of high basicity containing ten groups.

The formulations given above do not say anything collectively concerning the binding of the usually very numerous water molecules in the free acids and in many of their salts. However, a formal agreement in the water content of the various limiting acids is as well achieved in the one manner of writing as in the other, which is not the case in the formulation according to oxides¹⁰⁷.



The extensively dehydrated acids are not considered in this scheme¹⁰⁸.

In the formulation of the free acids as heteropolar compounds as given here, it is to be remembered that the ionizable hydrogen in acids never faces the anion as a proton, but, even when the free acid has a heteropolar structure, forms at least the hydroxonium ion H_3O^+ with one molecule of water. Or, like anhydrous sulphuric or nitric acid, for example, the acid is not at all heteropolar, but has the ionizable hydrogen homopolarly bound to the oxygen, though with a more or less strongly polar bond. With the extensively hydrated acids, it is to be assumed on account of their strength that a part at least of the acid hydrogen atoms should be written $[\text{H}_3\text{O}]$ instead of H in the formulae, the number of molecules of water being reduced correspondingly. But it may be considered at least doubtful whether, with basicities as high as the MIOLATI-ROSENHEIM theory requires, all the acidic hydrogen is present as hydroxonium groups.

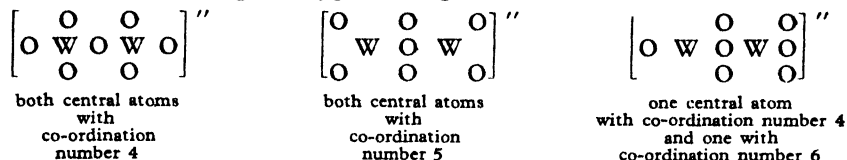
The formulae given above, no matter whether they are written according to MIOLATI and ROSENHEIM with the pyro-acid radicals or with the tri-acid radicals, require a still more extensive interpretation if they are not to remain merely a formal model. The structure of the complexes, even when the water content is at first disregarded, may be fashioned very differently according to the same written convention. The pyrotungstate radical $\text{W}_2\text{O}_7''$, for example, could be constructed according to the pattern of the pyrochromate

¹⁰⁶ P. SOUCHAY, *Bull. soc. chim. France*, 1942, [v], 9, 289, has shown that the high basicity is valid only for the acids with ten groups. The guanidinium salts of the limiting acids obtained by ROSENHEIM were in reality salts of the 10-acids.

¹⁰⁷ A. ROSENHEIM and J. JAENICKE, *Z. anorg. Chem.*, 1912, 77, 239; 1917, 100, 346.

¹⁰⁸ A compilation of all the hydrates known with certainty, in which older and not quite correct statements are reported, is given by O. KRAUS, *Naturwissenschaften*, 1937, 25, 250 (cf. p. 187 ff.).

ion (p. 155), both central atoms having the co-ordination number 4, or alternatively with multiple oxygen bridges:



Finally the pyrotungstate radicals need not be independent but could also be held together by oxygen bridges. On account of the different possibilities, the fact that so far no pyro-anions have been detected in acid solutions of tungstates¹⁰⁹ and molybdates¹¹⁰, but, in addition to the parent ion, only isopoly-acid complexes of higher molecular weight, is not necessarily¹¹¹ to be brought forward against the inclusion of possibly modified pyro-acid complexes within the complex of a crystalline compound, especially since pyrotungstates and pyromolybdates are also known¹¹².

With the assumption of four tri-acid radicals, $\text{W}_3\text{O}_{10}''$ or $\text{Mo}_3\text{O}_{10}''$ ¹¹³, the possibilities become still more numerous. A spatial interpretation of the complex formulae thus appears hopeless in every case on account of the lack of data. MIOLATI and ROSENHEIM have therefore desisted from providing one. The scheme they give must remain formal and even unproved with regard to the fundamental assumptions of the co-ordination number 6 and of the pyro-acid radicals.

L. C. PAULING introduced new viewpoints for a spatial interpretation of complexes¹¹⁴, in which he utilized the atomic distances determined by X-ray analysis for other compounds, especially the silicates. Since his ingenious construction, for which he also utilized the water molecules, was proved incorrect a few years later by X-ray analysis, and is furthermore irreconcilable with the existence of anhydrous salts and acids poorer in water (p. 187), only the basic ideas will be sketched here. These have provided valuable hints for structure analysis by X-rays.

PAULING considered the complex as built up of ions of definite radii, that is, W^{6+} or Mo^{6+} for the positive central ion together with negative oxygen ions. The radii are derived from the lattices of oxides which — and this is certainly not strictly correct and in many cases can be seriously doubted

¹⁰⁹ G. JANDER, D. MOJERT and T. ADEN, *Z. anorg. Chem.*, 1929, **180**, 129; G. JANDER and W. HEUKESHOVEN, *ibid.*, 1930, **187**, 60; G. JANDER and H. WITZMANN, *ibid.*, 1933, **214**, 145; 275.

¹¹⁰ G. JANDER, K. F. JAHR and W. HEUKESHOVEN, *Z. anorg. Chem.*, 1930, **194**, 383; G. JANDER and H. WITZMANN, *ibid.*, 1933, **215**, 310.

¹¹¹ G. JANDER and K. F. JAHR, *Kolloid-Beihfte*, 1935, **41**, 342, are also unable to reject the possibility completely.

¹¹² F. HOERMANN, *Z. anorg. Chem.*, 1928, **177**, 145; E. CARRIÈRE, H. GUITER and R. GIACOMINI, *Bull. soc. chim. France*, 1943, [v], **10**, 587.

¹¹³ Trimolybdic acid, in contrast to pyromolybdic acid, is to be assumed a relatively stable intermediate stage in the polymerization of molybdic acid on acidifying in aqueous solution: G. JANDER and H. WITZMANN, *Z. anorg. Chem.*, 1933, **215**, 316; G. JANDER, K. F. JAHR and H. WITZMANN, *ibid.*, 1934, **217**, 65; G. JANDER and K. F. JAHR, *Kolloid-Beihfte*, 1934, **41**, 27.

¹¹⁴ L. C. PAULING, *J. Am. Chem. Soc.*, 1929, **51**, 2868.

(Chapter VIII, 5, (i)) — are regarded as ionic lattices. From the ratio of the radii of the positive and negative ions, the co-ordination number of the former, when one positive ion is surrounded by a number of negative ions, follows from an empirical rule of GOLDSCHMIDT¹¹⁵. From available observational data, PAULING derived the co-ordination number 6 for molybdenum and tungsten with respect to oxygen¹¹⁶, so that the molybdic and tungstic acid radicals have thus the octahedral structures MoO_6 and WO_6 . However, this can be brought into line with the number of oxygen atoms present in the complex only if the radicals are not isolated, but are linked together in a ring by means of oxygen bridges. At the centre of the ring there is then room for a tetrahedral XO_4 ion of valency $-(8-n)$, where n is the valency of the central atom X. Accordingly the basicities of the acids, which correspond to the primary basicities of COPAUX, are calculated exactly as usual by assuming the co-ordination number 4 for the central atom.

As already stated, X-ray analysis has not confirmed PAULING'S structure, but proved correct only some of the basic ideas it contained, namely the octahedral MoO_6 and WO_6 groups and their linking through oxygen bridges in a large ring-shaped structure. This point is most clearly illustrated by the fact that even the inclusion of new determinations with the old has not sufficed to give the structure of the complexes with even moderate certainty. The possibilities which remain are still too many. The position is the same as in organic chemistry when the reactions of a compound are not sufficient for a moderately certain structural formula to be derived from them, except that here the pieces of evidence which are to be brought forward in favour of a particular structure are naturally of a different kind.

Even X-ray analysis has not so far been able to answer all constitutional questions. The structure is only known with certainty for the limiting acids with twelve MoO_3 or WO_3 groups¹¹⁷. Here the central atom is tetrahedrally surrounded by four oxygen atoms which simultaneously belong to more than one MoO_6 or WO_6 octahedron¹¹⁸. These octahedra make contact partly by their edges and partly by their faces, enclosing the central tetrahedron within a spatially constructed, wreath-like, cyclic structure as shown in Fig. 24¹¹⁹. This structure has been determined for numerous heteropoly-

¹¹⁵ V. M. GOLDSCHMIDT, *Ber.*, 1927, **60**, 1263. Cf. Chapter VIII.

¹¹⁶ That this conclusion is not compelling results from the existence of the WO_4 ion in the lattices of tungstates, e.g., of scheelite CaWO_4 .

¹¹⁷ J. F. KEGGIN, *Nature*, 1933, **131**, 908; **132**, 351; *Proc. Roy. Soc.*, 1934, **A 144**, 75; J. W. ILLINGWORTH and J. F. KEGGIN, *J. Chem. Soc.*, 1935, p. 575; A. J. BRADLEY and J. W. ILLINGWORTH, *Proc. Roy. Soc.*, 1936, **A 157**, 113; R. SIGNER and H. GROSS, *Helv. chim. Acta*, 1934, **17**, 1076 (silico- and borotungstic acids, metatungstic acid).

¹¹⁸ In the structure drawn up by PAULING, the tetrahedron lay free inside a ring formed by octahedra. The individual octahedra made contact by corners and edges but not by faces.

¹¹⁹ K. F. JAHR has suggested a somewhat modified structure in order to explain the hydrolysis of phospho-12-tungstic acid to hexatungstic acid and phospho-6-tungstic acid: *Naturwissenschaften*, 1941, **29**, 531. The WO_6 octahedra are thereby less distorted, having edges and not faces in common. See in this respect H. O'DANIEL, *Z. Krist.*, 1942, **104**, 225.

acids and their salts¹¹⁷. So far as it has not been derived directly from X-ray exposures, it can be inferred from isomorphous relationships¹²⁰.

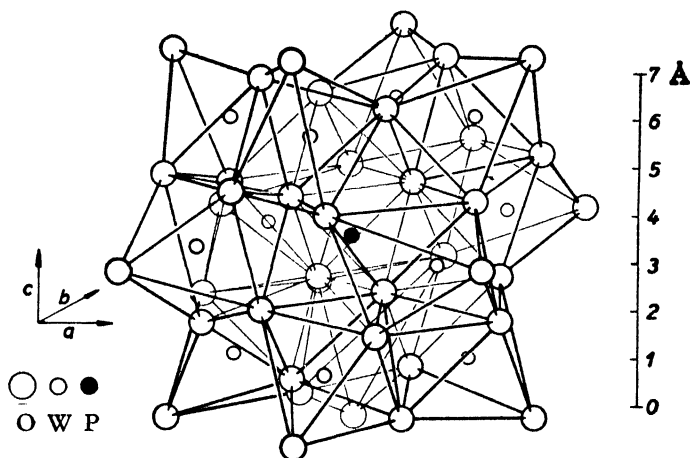
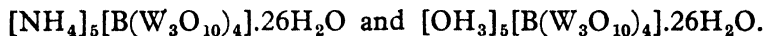


Fig. 24. Lattice of the anion of phosphotungstic acid $[P(W_3O_{10})_4]^{3-}$. The phosphorus atom, which is indicated as a black dot at the centre of the figure, is tetrahedrally surrounded by four oxygen atoms at a distance of 1.71 Å. (In the phosphate ion the distance is appreciably smaller at 1.5 Å.) The oxygen atoms are to be thought of as situated at the corners of octahedra. The tungsten atoms are situated at the centres of the octahedra. (One of these tungsten atoms lies right at the back and is not to be seen in the Figure.)

The binding of the water molecules is to be derived only in part from the X-ray exposures, as in phosphotungstic acid $H_3[P(W_3O_{10})_4] \cdot 29H_2O$, where the positions of the water molecules of the cation $[H_3 \cdot 29H_2O]^{3+}$ are indeed known, but not those of the protons which give it the charge¹²¹. The isomorphism between various free acids and many of their salts (p. 184 ff), e.g., between borotungstic acid and its ammonium salt, and the identity of their X-ray interferences leave no doubt that in such cases a part of the water present is bound in hydroxonium ions¹²²:



The number of water molecules bound in hydroxonium ions never exceeds the basicity of the acid. In addition, the lattices formed by large complex anions are so spacious that, apart from the cations, water molecules can also find room in their unoccupied spaces.

¹²⁰ Isomorphous relationships by reason of X-ray analyses: O. KRAUS, *Z. Krist.*, 1935, **91**, 402 (silico- and borotungstic acids and ammonium borotungstate); 1936, **94**, 256 = *Fortschr. Min. Krist. Petr.*, 1937, **21**, 63 (various silico- and borotungstates, dependence of the lattice type on the cation, exchange possibilities of cations with respect to water); *Z. Krist.*, 1936, **93**, 379 and 1937, **96**, 330 (regular and triclinic $M^{III}H[Si(W_3O_{10})_4] \cdot 28$ or $20 H_2O$); 1939, **100**, 394 (14-hydrates of $H_4[Si(W_3O_{10})_4]$ among others, Li, Hg and Tl salts); *Naturwissenschaften*, 1937, **25**, 250 (free acids, various hydrates).

¹²¹ A. J. BRADLEY and J. W. ILLINGWORTH, *Proc. Roy. Soc.*, 1936, **A 157**, 113.

¹²² O. KRAUS, *Z. Krist.*, 1935, **91**, 402.

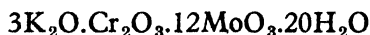
If the structures which have now been fixed for the limiting acids are compared with the older formulations, that in which the central atom appears with the co-ordination number 4 seems to be the most appropriate. It exhibits the correct co-ordination number and indicates the preferentially observed basicity. That to which it does not give proper expression is the coherence of the tri-acid groups $(W_3O_{10})_4$ and $(Mo_3O_{10})_4$, which do not possess the independence one might be inclined to assume from the formulae. But it is impossible to reflect this coherence in a formula which is not spatially constructed.

With respect to the success of X-ray analysis among the heteropoly-acids, one must not forget that it has so far provided an extensive structural clarification for only a single class of compounds, namely that of the limiting acids.

Although extensive, this clarification is still not complete, for the question of the cause of the isomerism between silicotungstic and tungstosilicic acids, significant from a structural-chemical standpoint, can still not be answered. The X-ray analysis of tungstosilicic acid and its salts is still lacking. Furthermore, MIOLATI and ROSENHEIM also had to pass over this question, since their theory offers nothing more definite towards an explanation than the structure determinations which are so far available.

It is not yet known how the acids which contain only ten or nine MoO_3 or WO_3 groups respectively on a central atom are constructed. One can of course imagine two or three acid groups broken out of the wreath of MoO_6 or WO_6 octahedra, but the question *where?* remains, if indeed the relationships between the acids containing twelve, ten and nine such groups are so simple. These also remain unclarified, inasmuch as the high basicity which doubtless occurs with the 10-acids does not exist in the 12- and 9-acids. The 1:11-, 2:17-, 2:21- and similar acids, which are considered by ROSENHEIM to be dinuclear, cannot be derived from the spatial structure of the 12-acids without arbitrariness. However practical this conception may appear from the formal standpoint, their dinuclear nature is not to be regarded as proved, since structure analyses by X-rays have not yet been carried out.

The large class of weak heteropoly-acids with six MoO_3 groups on a central atom, which are known only in their salts, *e.g.*,



(which is rose-red and arises by heating the potassium salt of paramolybdic acid with a solution of chrome alum), is likewise still not structurally elucidated. ROSENHEIM writes their structures analogously to the complex oxalates¹²³, *e.g.*, so that $K_3H_3[Cr(MoO_4)_6].3H_2O$ is analogous to $K_3[Cr(C_2O_4)_3]$, with the difference that the two co-ordination positions

¹²³ A. ROSENHEIM and H. SCHWER, *Z. anorg. Chem.*, 1914, **89**, 226.

occupied by one oxalate radical are each taken up by one molybdate radical in the molybdate complex. A structural model based on the limiting-acid type and containing the MoO_3 groups spatially arranged in contacting MoO_6 octahedra has been drawn up by ANDERSON¹²⁴, but experimental support for it is still lacking.

For the structures of the heteropoly-acids having compositions differing from those of the heteropoly-acids of molybdenum and tungsten, nothing definite can be inferred from the known structures of the limiting acids. This is true, for example, of the phosphovanadic acids, whose different compositions may be seen in the following salts, the deep-red so-called purpureo-vanadates¹²⁵:

$3\text{K}_2\text{O} \cdot 2\text{P}_2\text{O}_5 \cdot 8\text{V}_2\text{O}_5 \cdot aq$	$\text{P} : \text{V} = 1 : 4$	$\text{P} : \text{V}_8 = 2 : 1$
$10\text{SrO} \cdot \text{P}_2\text{O}_5 \cdot 8\text{V}_2\text{O}_5 \cdot aq$	1 : 8	1 : 1
$4(\text{NH}_2)\text{O} \cdot 2\text{P}_2\text{O}_5 \cdot 24\text{V}_2\text{O}_5 \cdot aq$	1 : 12	2 : 3
$5(\text{NH}_4)_2\text{O} \cdot 2\text{P}_2\text{O}_5 \cdot 24\text{V}_2\text{O}_5 \cdot aq$	1 : 12	2 : 3
$11\text{K}_2\text{O} \cdot 2\text{P}_2\text{O}_5 \cdot 24\text{V}_2\text{O}_5 \cdot aq$	1 : 12	2 : 3
$10\text{K}_2\text{O} \cdot \text{P}_2\text{O}_5 \cdot 24\text{V}_2\text{O}_5 \cdot aq$	1 : 24	1 : 3
$10\text{BaO} \cdot \text{P}_2\text{O}_5 \cdot 24\text{V}_2\text{O}_5 \cdot aq$	1 : 24	1 : 3

Here also the ratio 1 : 12 occurs. However, the additional ratios 1 : 6, 1 : 9 and 1 : 10 which occur in the phosphomolybdic and phosphotungstic acids are not found, but instead 1 : 4 and 1 : 8. For reasons which will be discussed in the section on isopoly-acids (pp. 204, 210) an octovanadic acid is to be assumed as the structural unit in these purpureo-vanadates. The so-called phosphates of luteo-vanadic acid, in which the P : V ratio is 1 : 1 or 1 : 2, are not salts of heteropoly-acids but alkali vanadium phosphates containing the vanadium ion $\text{V}^{\text{VO}}\cdots$ analogous to the vanadyl ion $\text{V}^{\text{IV}}\text{O}\cdots$. The alkali-free compound $\text{V}_2\text{O}_5 \cdot \text{P}_2\text{O}_5$ is not a heteropoly-acid, but vanadium phosphate $(\text{VO})\text{PO}_4$ ¹²⁶.

The ratios preponderating in the phosphovanadic acids lead to the isopoly-acids. Among the acids of molybdenum and tungsten are also compounds which indicate that close relationships exist between heteropoly-acids and certain isopoly-acids. This is especially true of the so-called metatungstates which, precisely on account of these relationships, are reckoned among the heteropoly-acids¹²⁷. They are in fact isomorphous with the silicotungstates. Metatungstic acid itself is isomorphous with the trigonal series of phospho-, silico- and borotungstic acids. The salts are obtained from the normal tungstates by the *gradual* addition of hydrochloric acid, whereupon the tungstic acid which first separates gradually redissolves. They have the composition $\text{M}_2\text{O} \cdot 4\text{WO}_3 \cdot n\text{H}_2\text{O}$. The free acid $4\text{WO}_3 \cdot 9\text{H}_2\text{O}$ is formed from its barium salt and the calculated quantity of sulphuric acid.

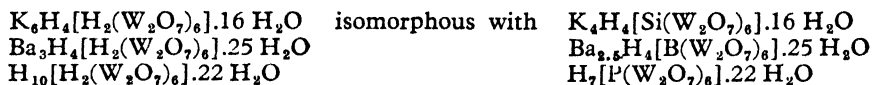
¹²⁴ J. S. ANDERSON, *Nature*, 1937, **140**, 850.

¹²⁵ G. JANDER, K. F. JAHR and H. WITZMANN, *Z. anorg. Chem.*, 1934, **217**, 76.

¹²⁶ G. JANDER, K. F. JAHR and H. WITZMANN, *Z. anorg. Chem.*, 1934, **217**, 78.

¹²⁷ H. COPAUX, *Ann. chim. phys.*, 1909, [viii], **17**, 217; *Z. anorg. Chem.*, 1911, **70**, 299.

In order to express the isomorphism by similar structural formulae, COPAUX¹²⁸, since a hetero central atom is lacking in metatungstic acid, placed hydrogen in its stead. This, based on the incorrect MIOLATI-ROSENHEIM theory which he used, yielded the following formulae:



The water written separately can be removed at 110—120° without far-reaching change, the remaining water cannot¹²⁹. The basicity of metatungstic acid does not by any means correspond to the ten hydrogen atoms written as cations. Rather the acid is only hexabasic. This is not surprising now that the incorrectness of the MIOLATI-ROSENHEIM theory and its experimental support is known.

ROSENHEIM¹³⁰ has extended COPAUX's hypothesis to the polymolybdates and polyvanadates, which he derived from the hypothetical complex aquo-acids $\text{H}_{10}[\text{H}_2\text{O}_6]$, $\text{H}_8[\text{H}_2\text{O}_6]$ and $\text{H}_6[\text{H}_2\text{O}_4]$ and denoted as "aquates".

The substitution of the central atom in the complex by hydrated hydrogen, as is undertaken here by COPAUX and ROSENHEIM, means in the last resort the dethronement of the central atom from its rôle of determining the structure of the heteropoly-acids. Consequently it is more or less tacitly admitted that the coherence of the acid radicals surrounding the central atom according to the modern knowledge of structure, that is to say, the *wreath*, is the essential thing. The wreath holds together even when the centre is removed. If in its place the hole is simultaneously filled up with hydrated hydrogen, it is still not very obvious that this should hold the structure of the complex together. Since it is now known by reason of X-ray analysis that the tungstate radicals in the wreath of metatungstic acid are held together in the same way as in the heteropoly-acids, no artificial assumption is henceforth necessary concerning the structure of a centre which governs the construction. By way of example, it is perhaps sufficient to assume that in metatungstic acid the place of the silicon atom in silicotungstic acid has been taken by four hydrogen atoms which attach themselves to the four oxygen atoms previously linked to the silicon. A tetravalent anion $[\text{H}_4\text{W}_{12}\text{O}_{40}]^{4-}$ would then result for metatungstic acid, which may be thought of as united in a saltlike manner to four hydroxonium ions:



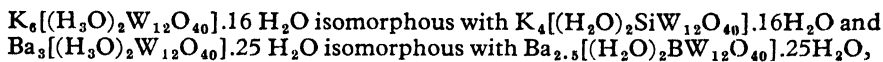
Or one might assume that at the centre, in place of the central atom, only two hydrogen atoms link up with two oxygen atoms: the anion of metatungstic acid would then be hexavalent and written $\text{H}_2\text{W}_{12}\text{O}_{44}^{6-}$. If necessary,

¹²⁸ H. COPAUX, *Ann. chim. phys.*, 1909, [viii], 17, 217.

¹²⁹ A. ROSENHEIM, *Z. anorg. Chem.*, 1915, 93, 280; 1916, 96, 144—145 (footnote 1).

¹³⁰ A. ROSENHEIM and J. FELIX, *Z. anorg. Chem.*, 1913, 79, 299; A. ROSENHEIM, *ibid.*, 1916, 96, 151; 175; A. ROSENHEIM and J. JAENICKE, *ibid.*, 1917, 100, 343.

hydration of the central hydrogen atoms would again still have to be reckoned with. Such a hexavalent anion of metatungstic acid would agree with the composition of the salts



especially since these salts at 100—120° lose only 16 or 25 molecules of water respectively¹³¹. It is self-evident that such formulations are speculative, since various possibilities are conceivable for the linking of the hydrogen atoms and water molecules. However, they are not this to the same degree as the formulations of COPAUX and ROSENHEIM. Above all, an unprejudiced judge will not lose the feeling that, in the generalization in which the last of COPAUX's concepts partakes, an empty formalism is schematically applied far beyond the limits of experimentally determined facts.

Holding fast to COPAUX's idea that the central atom in heteropoly-acids does not in reality play the supreme rôle that it otherwise does in complex compounds, the wreath formed from radicals of the same acid appears as an *isopoly-acid complex* determining the structure of the whole complex. Connections between the structures of heteropoly-acids and isopoly-acids would then be expected. Thus it is possible not only to be led from the heteropoly-acids to the isopoly-acids, as is the case here, but also by the study of those isopoly-acids whose acid radicals can also serve as constituents of heteropoly-acids from the isopoly- to the heteropoly-acids. G. JANDER has followed up this line of thought in numerous investigations, and thereby greatly enriched our knowledge of the isopoly-acids.

6. Isopoly-acids

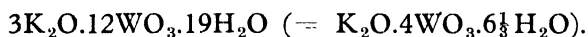
As has already been noted, the isopoly-acids do not provide in their analytical composition any kind of indication of a particular structure. Accordingly, in his investigations on the isopoly-acids, JANDER did not proceed from structural-chemical viewpoints, but from the outset struck a fundamentally different path. It is the way which is indicated for the unprejudiced analyst, who for so long has had completely to forgo all structural-chemical conceptions, since he did not see any path to a planned degradation or planned synthesis of the compounds with which he worked. He commenced his task not with the object of creating a systematization of the substances, but observed the behaviour of the substances and that concerning them which was adaptable to research. Before discussing JANDER's investigations, of which he himself has provided a thoroughly comprehensive presentation¹³², a brief characterization of some of the isopoly-acids will be given, beginning with metatungstic acid. In this we will confine ourselves essentially to the isopoly-acids of tungsten, molybdenum and vanadium.

¹³¹ Potassium salt: A. ROSENHEIM and J. JAENICKE, *Z. anorg. Chem.*, 1917, **101**, 242. Barium salt: A. ROSENHEIM, *ibid.*, 1916, **96**, 145 (footnote).

¹³² G. JANDER and K. F. JAHR, *Kolloid-Beihfte*, 1934, **41**, 1; 297.

(i) Polytungstates

Polytungstates arise on carefully acidifying normal tungstates, e.g., $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$, which have an alkaline reaction in consequence of hydrolysis. A white gelatinous precipitate of hydrated WO_3 is first formed, which however redissolves on shaking. According to the degree of acidification different polytungstates are obtained from the solutions¹³³. From weakly acid solutions of $p_{\text{H}} > 4$ *paratungstates* result, e.g., sodium paratungstate with the composition $5\text{Na}_2\text{O} \cdot 12\text{WO}_3 \cdot 28\text{H}_2\text{O}$; from more strongly acid solutions of $p_{\text{H}} < 4$ *metatungstates* are obtained which are richer in tungsten, containing namely four equivalents of tungstic acid to one of alkali, for example,



Strong acidification by more than one molecule of acid to one molecule of tungstate slowly precipitates the whole of the tungstic acid as hydrated tungsten trioxide.

Free metatungstic acid can be obtained exactly like the free heteropolyacids by shaking acidified metatungstate solutions (which cannot be kept indefinitely) with ether¹³⁴. All polytungstates contain much "water of crystallization".

(ii) Polymolybdates

The polyacids of molybdenum are more numerous than those of tungsten. By the acidification of solutions of the normal molybdates, polymolybdates can be obtained, whose content of molybdic acid increases with increasing hydrogen-ion concentration. Salts of the following types have been obtained in the crystalline state:

Paramolybdates. $3\text{Na}_2\text{O} \cdot 7\text{MoO}_3 \cdot 22\text{H}_2\text{O}$; $3(\text{NH}_4)_2\text{O} \cdot 7\text{MoO}_3 \cdot 4\text{H}_2\text{O}$ ¹³⁵ (apparently not $5(\text{NH}_4)_2\text{O} \cdot 12\text{MoO}_3 \cdot 7\text{H}_2\text{O}$ ¹³⁶); the alkali salts are best obtained from molybdic acid and the calculated quantity of alkali hydroxide in the warm.

Trimolybdates. $\text{Na}_2\text{O} \cdot 3\text{MoO}_3 \cdot 7\text{H}_2\text{O}$; obtained from solutions of paramolybdates and acetic acid¹³⁷.

Tetramolybdates, also named *metamolybdates.* $\text{Na}_2\text{O} \cdot 4\text{MoO}_3 \cdot 8\text{H}_2\text{O}$; obtained from $\text{Na}_2\text{MoO}_4 \cdot x\text{H}_2\text{O}$ and 1.5 equivalents of HCl or HNO_3 ^{137, 138}.

¹³³ First observed by F. MARGUERITE, *Ann. chim. phys.*, 1846, [iii], 17, 475. Cf. also A. LAURENT, *ibid.*, 1847, [iii], 21, 54.

¹³⁴ M. SOBOLEW, *Z. anorg. Chem.*, 1896, 12, 29 (footnote); A. ROSENHEIM and F. KOHN, *ibid.*, 1911, 69, 253.

¹³⁵ According to the new analyses of I. LINDQVIST, *Acta Chem. Scand.*, 1948, 2, 88, which support the old formula of M. DELAFONTAINE, *J. prakt. Chem.*, 1865, [i], 95, 141; *Arch. sci. phys. nat.*, 1865, [ii], 23, 17; F. ULLIK, *Liebigs Ann. Chem.*, 1867, 144, 219. G. CARPÉNI (*Bull. soc. chim. France*, 1947, [v], 14, 492) leaves the question open. Cf. also J. H. STURDIVANT, *J. Am. Chem. Soc.*, 1937, 59, 630.

¹³⁶ A. ROSENHEIM, *Z. anorg. Chem.*, 1916, 96, 139.

¹³⁷ F. ULLIK, *Liebigs Ann. Chem.*, 1867, 144, 204; 320.

¹³⁸ G. WEMPE, *Z. anorg. Chem.*, 1912, 78, 298.

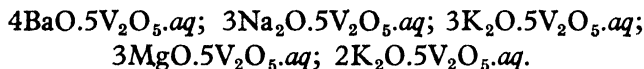
Octomolybdates. $\text{Na}_2\text{O} \cdot 0.8\text{MoO}_3 \cdot 17\text{H}_2\text{O}$; obtained from Na_2MoO_4 and 1.75 equivalents of HCl or HNO_3 ^{138, 139}.

*Decamolybdates*¹³⁹. $\text{Na}_2\text{O} \cdot 10\text{MoO}_3 \cdot aq$, in comparison with the octomolybdates relatively insoluble, and hexadecamolybdates¹⁴⁰ $\text{Na}_2\text{O} \cdot 16\text{MoO}_3 \cdot aq$ have also been obtained.

The tetramolybdates correspond to the metatungstates. Like them they contain one equivalent of alkali or alkaline-earth hydroxide to four of the acid. The content of water of crystallization is not always the same¹⁴¹.

(iii) Polyvanadates

Vanadic acid forms *ortho*-, *pyro*- and *metavanadates* which have been obtained crystalline as colourless salts. On acidification of their solutions, bright-orange to dark-red solutions are obtained from which, depending upon the concentrations of the added acid and of the solution, as well as upon the kind of cation and anion of the added acid, yellow, orange or red salts crystallize, usually with much water of crystallization. Their composition, measured by the $\text{M}^{\text{I}}_2\text{O} : \text{V}_2\text{O}_5$ ratio, varies within wide limits. Among others, the following ratios have been found: 6 : 7; 5 : 6; 4 : 5; 3 : 4; 2 : 3; 3 : 5; 4 : 7; 1 : 2; 3 : 7; 2 : 5; 1 : 3. If salts are allowed to crystallize from weakly acid solutions which contain 0.75 equivalents of acid to one of $\text{M}^{\text{I}}\text{VO}_3$ and have been allowed to stand for a long time, only orange salts are obtained, which according to their composition can be assigned to the one type $n\text{M}^{\text{I}}_2\text{O} \cdot 0.5\text{V}_2\text{O}_5 \cdot aq$, where n can be 2, 3 or 4¹⁴², examples being:



Since they all contain $5\text{V}_2\text{O}_5$ with varying amounts of base, they can be designated as *pentavanadates*.

From more strongly acid solutions, salts of different compositions are also obtained, e.g., $\text{K}_2\text{O} \cdot 3\text{V}_2\text{O}_5$ (anhydrous!), $3\text{BaO} \cdot 4\text{V}_2\text{O}_5 \cdot aq$ and $2\text{BaO} \cdot 3\text{V}_2\text{O}_5 \cdot aq$.

In the preparation of these salts as also of the pentavanadates, the solutions must have been allowed to stand for some time, usually several days, for, as indicated by the change of hydrogen-ion concentration with time¹⁴³, changes in the polyvanadate ions occur which require a considerable time for the establishment of the final equilibrium. Something similar is not observed with acidified molybdate and tungstate solutions; these react

¹³⁹ A. ROSENHEIM and J. FELIX, *Z. anorg. Chem.*, 1913, **79**, 292.

¹⁴⁰ F. ULLIK, *Liebigs Ann. Chem.*, 1870, **153**, 373.

¹⁴¹ Ultra-violet absorption of molybdates at various pH values and electrometric titrations: G. CARPÉNI, *Bull. soc. chim. France*, 1947, [v], **14**, 484; 490.

¹⁴² G. JANDER and K. F. JAHR, *Z. anorg. Chem.*, 1933, **211**, 49; K. F. JAHR and G. JANDER, *ibid.*, 1934, **220**, 201.

¹⁴³ With the aggregation to larger ions, H^+ is used up and H_2O formed, an example of the simplest case being $2\text{VO}_4^{\text{IV}} + 2\text{H}^+ \rightleftharpoons \text{V}_2\text{O}_7^{\text{IV}} + \text{H}_2\text{O}$.

practically instantaneously with the added hydrogen ions to form the poly-molybdate or polytungstate ion stable under the conditions concerned.

(iv) Methods for investigating the Isopoly-acids

The variety of the polyvanadates is such as to illustrate most clearly that any attempt to found a systematization upon the analytically determined compositions is hopeless. Resort must therefore be made to other methods of investigation. One is led to these by a different formulation of the problem. This runs: *In what way are the isopoly-acids formed in solution, how does the aggregational process proceed, and to isopoly-acid anions of how high a molecular weight does it lead under any exactly prescribed experimental conditions?* The advance which has been made by the experimental approach to this question is especially well illustrated by the example of the latterly discussed polyvanadates. But first the most important methods of investigation which have come to be applied to this problem will be collectively dealt with.

On account of the hydrolysis of the salts, the *molecular weights* of the isopoly-acid anions cannot be determined according to the usual classical procedures. Observations of the *rate of diffusion* do not yield an exact determination, but, for the immediate purpose, provide a completely adequate approximation for the molecular weight, which can be calculated by virtue of the relationship

$$D\sqrt{M} = \text{a constant}^{144}.$$

Here D is the *diffusion coefficient* which, according to FICK's law¹⁴⁵, is defined by

$$\Delta S = -D \cdot q \cdot \Delta t \cdot \frac{dc}{dx},$$

where q is the area of cross-section, dc/dx is the concentration gradient and ΔS the quantity of substance in moles which, with the gradient unity, diffuses through 1 cm² of a cylindrical diffusion vessel in the time Δt . The unit of time chosen for diffusion in liquids is usually the day. In order to make the rates of diffusion determined under different conditions strictly comparable, the diffusion coefficients are referred to a definite temperature, 10°, and multiplied by the experimentally determined specific viscosity of the solution z , thus: $D_{10} \cdot z$.

Objections can be raised against the strict validity of the equation given here as the basis of molecular-weight determinations, since it does not include the form of the diffusing molecules and ions, that is to say, their charge and their hydration, upon which the rate of diffusion without doubt also depends. The dimension $D\sqrt{M}$ will thus certainly not be a universal constant. The difficulties thereby involved can for the most part be avoided

¹⁴⁴ E. RIECKE, *Z. physik. Chem.*, 1890, 6, 564.

¹⁴⁵ A. FICK, *Poggendorffs Ann. Physik*, 1854, 94, 59.

if one compares the diffusion coefficients of the substances whose molecular weights are to be determined with the diffusion coefficients of chemically similar substances of known molecular weight. With ionizing substances, in addition, in order to eliminate the effect of electrostatic attraction between their cations and anions, the measurements are made in the presence of a large excess of an added, chemically indifferent electrolyte¹⁴⁶.

One control over the process of aggregation as determined by diffusion is the *measurement of light absorption*. Although it does not indicate the molecular weight, it does permit the appearance of different ionic species to be recognized. The best-known example is the change of colour which takes place when chromate solutions are acidified. Chromate, dichromate and polychromate ions can be clearly differentiated by the course of their absorption curves. For colourless ions, measurement must be made in the ultra-violet.

A further possibility of following the aggregation is provided by the *change in hydrogen-ion concentration*, since hydrogen ions are used up on aggregation and reformed on dispersion.

In addition to the study of the processes which take place in solution, the *compositions of the salts obtainable from solution* will naturally be drawn upon, as far as these crystallize homogeneously. But care must be exercised in drawing conclusions concerning the solutions from the crystalline salts and *vice versa*. They are by no means admissible when, in the case of slowly occurring aggregation and dispersion in solution, equilibrium has not been attained. As soon as final equilibrium has been achieved, the inferences in such cases will possess a certain conclusiveness. Conversely, if systems which aggregate rapidly are being studied, on crystallization an aggregation surpassing that in solution will possibly have to be reckoned with. It must be remembered that not only the hydrogen-ion concentration but also the concentration of the solution can of itself influence the composition of the compounds which crystallize out.

In the eventuality that equilibrium between the isopoly-acid anions for a given p_H is quickly reached, the changes taking place on varying the p_H can also be followed by *conductivity titrations* and *thermometric titrations*. Potentiometric titrations are usually unsuitable on account of the coexistence of different weak acids and bases whose salts undergo hydrolysis¹⁴⁷.

To these methods, always used with carefully considered criticism¹⁴⁸

¹⁴⁶ R. ABEGG and E. BOSE, *Z. physik. Chem.*, 1899, **30**, 545.

¹⁴⁷ For molybdates and tungstates, results agreeing with those obtained in other ways have been given: H. BRINTZINGER and C. RATANARAT, *Z. anorg. Chem.*, 1935, **224**, 100; H. BRINTZINGER and E. JAHN, *Z. anal. Chem.*, 1933, **94**, 396.

¹⁴⁸ JANDER's self-criticism was, however, not severe enough. More recent observations and critical considerations raised in conjunction therewith respecting the diffusion method and the interpretation of JANDER's experimental results show that caution is advisable respecting JANDER's conclusions, since some of them, as for example the existence of hexatungstic acid in solution and the assumption of an octovanadic acid as structural unit in purpureo-phosphovanadic acid, have turned out to be incorrect. Cf. P. SOUCHAY and S. DUBOIS, *Ann. chim.*, 1948, [xii], **3**, 88 (purpureo-vanadic acids); 105 (3-phosphotungstic acid).

by JANDER, is to be added the procedure utilized by BRINTZINGER¹⁴⁹ for the determination of molecular weights by dialysis. This has been applied to the problem of the isopoly-acids only for the molybdates and tungstates¹⁵⁰, where it has given results agreeing with those obtained by JANDER by other methods¹⁵¹.

(v) Isopoly-acids in Solution

Polyvanadates. — Acidified solutions of vanadates, within four regions of hydrogen-ion concentration well segregated from one another, possess diffusion coefficients which are clearly distinguishable. It is accordingly to be assumed that in each of these regions one particular isopoly-acid is intrinsically stable. From the calculation of the molecular weight, at $p_H \sim 12.5$ a mono-, from 11 to ~ 9.2 a di-, up to 7 a tetra- and up to 2.2 a pentavanadate anion is present (see Fig. 25). Likewise irregularities in the

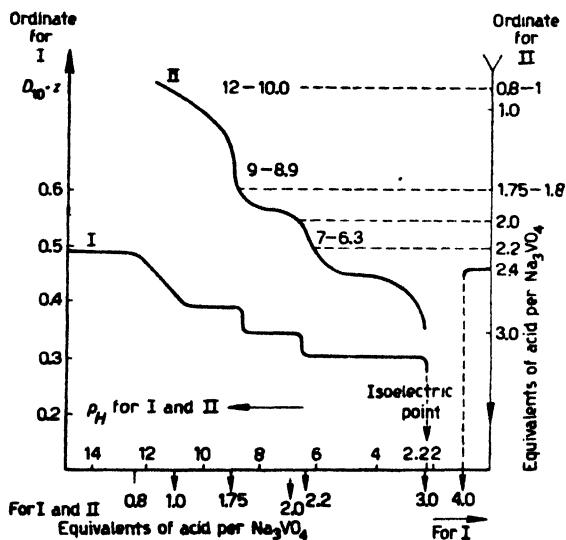


Fig. 25. (I) Diffusion coefficients of polyvanadates for varying p_H . (II) Hydrogen-ion concentration during the titration of polyvanadates.

hydrogen-ion concentration are observed in the same p_H regions during the addition of acid. Within the region in which an ionic species is stable, the hydrogen-ion concentration increases correspondingly with the quantity of acid added. Where an aggregation is occurring it remains constant in spite of continued addition, because the aggregation uses up hydrogen ions. The agreement with the results of diffusion experiments is visible in Fig. 25.

¹⁴⁹ H. BRINTZINGER, *Z. anorg. Chem.*, 1937, **232**, 415 (detailed description).

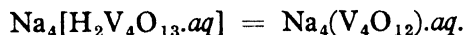
¹⁵⁰ H. BRINTZINGER and C. RATANARAT, *Z. anorg. Chem.*, 1935, **224**, 97.

¹⁵¹ Concerning the precision of the molecular weights determined by the dialysis process, see G. JANDER and H. SPANDAU, *Z. physik. Chem.*, 1939, **A 185**, 335.

If one considers the number of acid equivalents used up in attaining the individual stages, the following picture is obtained:

reaction	p_H region	moles H^+ per Na_3VO_4	increase for the particular step in aggregation	$\frac{H^+}{V}$
$2VO_4''' + 2H^+ = V_2O_7'''' + H_2O$	12—10.6	0.8 —1	1	1 : 1
$2V_2O_7'''' + 3H^+ = (HV_4O_{13})'''' + H_2O$	9— 8.9	1.75—1.8	$\frac{3}{4}$	3 : 4
$(HV_4O_{13})'''' + H^+ = (H_2V_4O_{13})''''$		2.0	$\frac{1}{4}$	1 : 4
$5(H_2V_4O_{13})'''' + 4H^+ = 4(H_3V_5O_{16})'''' + H_2O$	7— 6.8	2.2	$\frac{1}{5}$	1 : 5
$(H_3V_5O_{16})'''' + H^+ = (H_4V_5O_{16})''''$		2.4	$\frac{1}{5}$	1 : 5

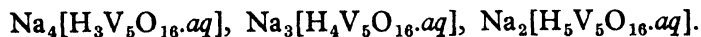
If the individual hydrogen-ion equivalents required are considered, a necessity for assuming acid isopoly-anions results. The relationships have been investigated in greater detail for the polymolybdic and polytungstic acids (pp. 207, 208). Crystallized salts are derived from the acid as well as from the neutral isopoly-anions. The close connection between salts, which were previously assigned to different types by reason of their analytical compositions, has now come to light through the behaviour of their anions on diffusion, and through the consumption of hydrogen ions on their formation. The so-called *metavanadates*, corresponding to their simple formulae, e.g., $NaVO_3$, do not contain the monomolecular metavanadate ion VO_3' , but a *tetrvanadate ion*:



These belong together with the 3 : 2- and 5 : 4-vanadates:



To the pentavanadates belong the 4 : 5-, 3 : 5- and 2 : 5-vanadates (p. 199):



The conclusions to be drawn from the observations are not exhausted with the recognition of the compositions of the isopoly-acid anions. In the formation of the aggregates, a characteristic difference in the rates of reaction is to be seen. Whereas those changes involving mono-, di- (pyro-) and tetra-vanadic acid, which take place in the alkaline region, proceed practically instantaneously, the conversion of tetra- to pentavanadic acid completes itself extraordinarily slowly. The chemical formulation is also in agreement with this difference. Tetrvanadic acid arises through a progressive polymerization of the ions — $VO_4''' \xrightarrow{H^+} V_2O_7'''' \xrightarrow{H^+} HV_4O_{13}''''$ — and *not* by a progressive linking up of vanadate ions, since otherwise a trivanadate ion would appear as an intermediate stage. It is consequently not to be expected that pentavanadic acid comes into existence by the simple addition

of a vanadate ion to tetravanadic acid, but rather that, continuing the polymerization series, a pairing up of the latter acid to octovanadic acid takes place. This conclusion is furthermore not unjustifiable, as a precise examination of the observations shows, for, if a colourless, not too dilute solution of sodium metavanadate, which thus in reality contains tetravanadate, is acidified, it turns dark brownish red in the first instance, but gradually pales in colour until it finally assumes the characteristic yellow colour of the pentavanadate ion. As long as the solution is a dark brownish red, it is decolorized again by alkali, whereas the yellow colour of the pentavanadate disappears again only very gradually on the addition of alkali. The brownish-red polyvanadate ion can be stabilized by phosphate ion¹⁵², and then exhibits a rate of diffusion corresponding to an octovanadate ion. Under special conditions, an octovanadate can be obtained crystalline from the solution¹⁵³. Moreover, this stabilized ion also undergoes immediate degradation by alkali to colourless ions. In the absorption of light, the octovanadate ion is characteristically different from the other polyvanadate ions. With increasing aggregation, as also in other cases such as the chromates, the absorption is displaced towards longer wave-lengths, while the absorption maximum, which here is situated in the ultra-violet, simultaneously decreases in intensity and steepness. This fact also speaks for a highly aggregated ion in the dark-brown solution. Admittedly, no special arrangement for pentavanadic acid is to be inferred from the light absorption.

The yellow pentavanadate ion is only formed with certainty after the formation of the octovanadate ion. Whether it arises from this by hydrolytic degradation, or owes its existence to a slow progressive conversion of tetravanadate ions with the monovanadate ions still occurring as traces in equilibrium, or whether it is ultimately formed from other ions in equilibrium in small quantities with the tetravanadate ions, must for the time being remain an open question, as long as it has not been decided whether the formation of the octovanadate ion, which rapidly reaches equilibrium with its products of degradation, is an intermediate process in the formation of the pentavanadate ion or a competing side reaction. In the slow degradation of the pentavanadate ion by the hydroxyl ion, which may of course proceed differently from its formation, the octovanadate ion has not so far been observed.

The great stability of pentavanadic acid towards alkali, by which it is differentiated from all the other polyvanadic acids, suggests that a structure must be assigned to it which differs from the others. However, there is so far no kind of reliable evidence for such a structural difference.

The pentavanadates are not stable towards hydrogen ions. On strong

¹⁵² For further concerning this stabilization, see p. 210.

¹⁵³ It is a sodium vanadium octovanadate $2\text{Na}_2\text{O} \cdot 9\text{V}_2\text{O}_5 \cdot aq$; cf. the mixed vanadium pentavanadates (p. 205): G. JANDER, K. F. JAHR and H. WITZMANN, *Z. anorg. Chem.*, 1934, 217, 65.

acidification their colour changes to a pale yellow, and the forementioned (p. 199) vanadium-rich salts $K_2O \cdot 3V_2O_5$, $3BaO \cdot 4V_2O_5$ and $2BaO \cdot 3V_2O_5$, among others, crystallize out from the solutions. The loss in colour points to a degradation, and the observed diffusion coefficients agree almost exactly with those which are found for the monovanadate ion in strongly alkaline solutions. An explanation for this apparently paradoxical ascertainment is provided by the fact that the iso-electric point is attained at a p_H of 2.2, where the solution is unstable and gradually precipitates hydrated vanadium pentoxide. After overstepping this point, at a p_H of less than 2, the solutions once again become stable and contain now instead of the aggregated, negatively charged poly-anions the monomolecular vanadium-containing cation VO_2^+ or VO^{\dots} ¹⁵⁴. The process is analogous to the transition of uranates into uranyl salts on acidification. The strangely constituted salts obtained from strongly acid solutions are the salts of one of these vanadium cations and alkali or alkaline-earth ions with the anion of pentavanadic acid, that is, mixed salts, e.g., $2BaO \cdot 3V_2O_5 = [Ba_2VO][V_5O_{16}.aq]$ or $[Ba_2VO_2][H_2V_5O_{16}.aq]$, which, on account of their relatively low solubility, escape further changes and are consequently easily isolated. The strongly acid vanadates listed on page 199 may also be spoken of as salts of this type, although here the proof for such a conception has not yet been supplied.

Polytantalates¹⁵⁵. — In connection with the vanadates, it may be briefly mentioned that tantalic acid forms a pentatantallic acid corresponding to pentavanadic acid, but, in contrast to vanadic acid, even in strongly alkaline solution. Monotantalates, in accord with diffusion measurements, cannot be obtained from aqueous solutions. The soluble potassium salt corresponds to the formula $7K_2O \cdot 5Ta_2O_5 \cdot 24H_2O$, and the difficultly soluble sodium salt $7Na_2O \cdot 5Ta_2O_5$ forms two hydrates with 22 and $30H_2O$, of which the latter corresponds to the crystalline form of sodium pentavanadate. Even in quite weakly acid solution tantalates are no longer stable, and at a p_H of less than 6 they precipitate gelatinous tantalic acid = hydrated tantalum pentoxide.

Polymolybdates. — The complicated processes involved in the aggregation of vanadate ions have already indicated all the essentials which can be gathered from JANDER's observations. For the polymolybdates and polytungstates, a brief presentation of the experimental results and their correlation with the classification of the molybdates undertaken according to their composition will therefore suffice. From Fig. 26 (p. 206) the following may be seen:

In alkaline solution up to the neutral point, the same ions diffuse. As is shown by a comparison with other ions, which cannot be inferred from

¹⁵⁴ Proof by transport measurements: P. DÜLLBERG, *Z. physik. Chem.*, 1903, **45**, 129.

¹⁵⁵ G. JANDER and H. SCHULZ, *Z. anorg. Chem.*, 1925, **144**, 225.

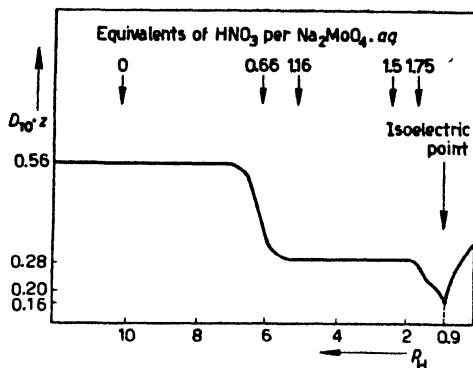


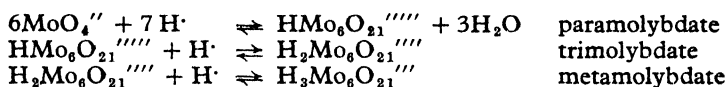
Fig. 26. Diffusion coefficients of the polymolybdates.

the figure, these must be ordinary molybdate ions. Between p_H values 7 and 5 a fall in the diffusion coefficient begins, which then again remains constant from p_H 5 to p_H 1.75. In this broad region the rate of diffusion corresponds to a *hexamolybdate* ion. It then falls again with a small inflection at p_H 1.5 to 1, corresponding to a *dodecamolybdic acid*. Solutions which have a p_H of 0.9 are unstable, and precipitate molybdenum trioxide in the course of time. The iso-electric point is reached with two moles of HNO_3 to one of Na_2MoO_4 . During the short time in which such solutions endure, a diffusion coefficient is observed which would correspond to a molybdate aggregated almost 24-fold.

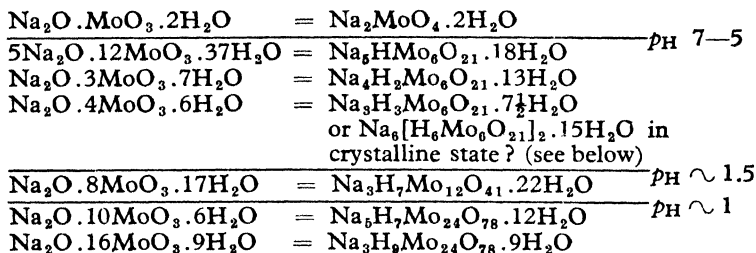
In the main, therefore, of the poly-acids only *hexamolybdic acid* exists. Evidence has been given for the existence of a *trimolybdic acid* in the p_H range 7 to 5, which is referred to here only for the sake of completion¹⁵⁶. From the various compositions of the different polymolybdates which crystallize within the region of existence of hexamolybdic acid according to the hydrogen-ion concentration, several polymolybdic acids might have been expected. The necessity for assuming isopoly-acid anions is even clearer than in the case of the polyvanadates (p. 203). Since here the region of existence of an acid of definite molecular weight is much broader than among the polyvanadates, the individual stages in the consumption of hydrogen ions can be more precisely defined. This can be accomplished by thermometric or conductometric titration. Changes in the temperature rise of the titrated solution indicate the formation of hexamolybdic acid and dodecamolybdic acid with the consumption of 7 and 9 equivalents of acid respectively per hexamolybdate ($= 6\text{Na}_2\text{MoO}_4$). The iso-electric point is reached with 12 equivalents. Each time an aggregation of the anion is under way, the temperature rise is greater than usual. The aggregations are thus exothermic processes. The individual intermediate stages of the acid isopolymolyb-

¹⁵⁶ The evidence has been compiled by G. JANDER and K. F. JAHR, *Kolloid-Beihfte*, 1934, 41, 34–35. Cf. also p. 191, footnote 113.

dates are thermochemically not particularly obvious. Thus between the para- and metamolybdates lies the trimolybdate, which is now recognized as an acid hexamolybdate:



According to JANDER, the formulae of the originally mentioned sodium polymolybdates (p. 198 ff) become the following:



Against the transference of the formulae derived for the aggregated ions in aqueous solution to crystalline salts, certain objections may be upheld. These will be brought into the discussion later.

Polytungstates. — For the tungstates, a demonstrable region of existence, besides that of the tungstate ion WO_4'' in strongly alkaline solution, belongs only to the hexatungstate ion between p_{H} 6 and p_{H} 1.5. The corresponding features of the curves of the diffusion coefficients and of conductometric and thermometric titrations, of which the two former are reproduced here (Fig. 27 and 28), indicate this directly. In the titrations, as with the molybdates, breaks in the curves are observed at 7 and 9 equivalents of acid, that is, with occurring aggregations.

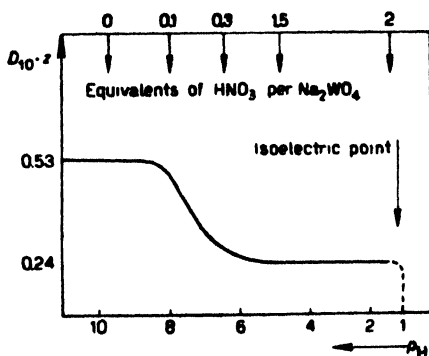


Fig. 27. Diffusion coefficients of polytungstates.

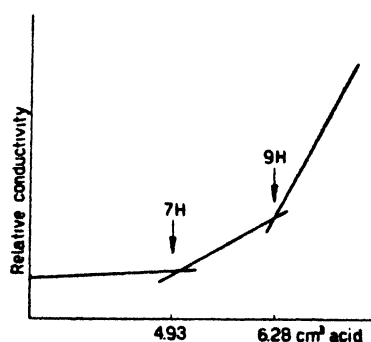
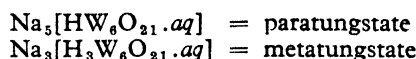


Fig. 28. Conductometric titration of polytungstates.

Paratungstates crystallize from solutions whose p_{H} is about 6 and in which there are 7 equivalents of $\text{H}\cdot$ to $6\text{WO}_4''$, and metatungstates from

solutions of p_H about 4 with 9 equivalents of H^+ to $6WO_4''$. Since in the solution only the hexatungstate ion can be detected, JANDER formulates the salts as acid hexatungstates, as for the molybdates:



As in the case of the various polymolybdates, it appears that here also the transference of the formulae valid for the ions in solution to the crystalline salts without any stipulations is not justifiable. Crystallization will of course certainly not involve any desired kind of aggregation or degradation of the ions occurring in solution, but, at least for ions with a pronounced region of stability, a definite relationship will exist between the ion in solution and that in the crystal lattice of the salt. It is thus perfectly possible for two ions from the solution to occur in the crystal. For example, the formula for sodium metamolybdate $Na_3H_3Mo_6O_{21}.7\frac{1}{2}H_2O$ with $7\frac{1}{2}$ molecules of water must apparently be doubled on account of the halving of a water molecule. A similar doubling of the formulae for the metatungstates is quite certainly to be undertaken, because here an analysis of the crystal structure is available which unambiguously indicates an anion consisting of twelve tungstate groups. The crystallized metatungstates are thus to be written $Na_6[H_3W_6O_{21}.aq]_2$ or, if one considers that a further molecule of water within the anion is separated during crystallization $Na_6[HW_6O_{20}.aq]_2 = Na_6[H_2W_{12}O_{40}.aq]$.

Since the experiments of JANDER indicate aggregates of ions in solution which bear a simple stoichiometric relationship to the sizes of the ions determined for some crystal lattices, the experimental results obtained in very different ways fit in with one another in the most satisfactory manner. This is particularly well illustrated on comparing the formula given here for the metatungstates with that derived from considerations of the crystal structure (p. 196).

To be sure, certain gaps in the experimental evidence still remain. In particular, an X-ray analysis of the crystal structure is lacking in most cases. In the investigations of the aggregation processes in solution, it appears especially dissatisfying that in the case of the tungstates no intermediate stages between mono- and hexatungstic acid have been demonstrated, although such must be assumed for reaction-kinetic reasons, namely the ditungstate ion¹⁵⁷ formed initially in bimolecular reactions. But to all appearances, in contradistinction to hexatungstic acid, these intermediates undergo change so readily that their existence shows itself only in the gradual fall of the diffusion coefficient between p_H 8 and p_H 6. This different behaviour from that of hexatungstic acid is suggestive of a different kind of structure

¹⁵⁷ A ditungstate $Na_2W_2O_7$ has been established by potentiometric titration and the formation of $Na_2W_2O_8$ with H_2O_2 : G. BIEHLER, *Ann. chim.*, 1947, [xii], 2, 489. In ammoniacal solution, on the other hand, the formation of W_2O_7'' could not be demonstrated.

— possibly chain-formation, whereas the hexatungstate ion may have a ring-shaped structure — as may also be suspected for pentavanadic acid with respect to the other polyvanadic acids. But even moderately certain evidence for the following up of such a hypothesis is lacking, as much in the one case as in the other.

(vi) Relations between Isopoly-acids and Heteropoly-acids

In connection with his investigations on the origin of isopoly-acids in solution, JANDER has also attempted to investigate the formation of heteropoly-acids by the same methods. The experiments are very similar in detail to those carried out on the isopoly-acids. Only the conclusions drawn from them will be discussed here, therefore.

The addition of a salt of an acid, which with the acid forming isopoly-acid anions can give a heteropoly-acid, scarcely affects the diffusion coefficients of the anions of the isopoly-acids in the alkaline region and in the region of moderate hydrogen-ion concentration. The same aggregation thus takes place here as occurs on acidifying a pure salt of the acid capable of forming isopoly-acids. This has been ascertained for the addition of periodates, phosphates and arsenates to tungstates, and of phosphates to molybdates and vanadates. Thus, in no case is the heteropoly-acid formed by a number of acid radicals of one acid grouping themselves in turn around a central atom, but in the middle p^H values the radicals first form themselves into stable isopoly-acid anions, that is, those of hexatungstic, hexamolybdic and tetravanadic acids. The presence of the foreign acid only makes itself noticeable at higher hydrogen-ion concentrations. At the iso-electric point the solutions are no longer unstable as in the case of the pure isopoly-acids, but completely stable, because now the stable heteropoly-acid has been formed with the other acid. Even at lower hydrogen-ion concentrations heteropoly-acid anions are also formed, but in equilibrium with their dissociation products, such being also present, especially in the case of a weak complex heteropoly-acid like periodotungstic acid. In the cases of the appreciably more stable phosphotungstic and phosphomolybdic acids, as shown by the large decrease in the diffusion coefficient of the phosphate ion, the disintegration of the complex is very slight, even at p^H 4. With these acids a further sinking of the diffusion coefficient below that of the hexapoly-ion is observed the other side of the iso-electric point, an indication that the phosphoric acid here enters into complex-formation with more than six tungstate radicals. In the case of the phosphomolybdic acids this can be directly observed in the increasing yellow colour of the solution, since the light absorption is displaced with increasing aggregation to the longer wave-lengths (p. 201). Since the hexa-isopoly-ions are so stable, one will not go wrong in seeing in the newly arisen aggregate a phospho-di-hexa-isopoly-acid, that is, a phospho-12-tungstic or phospho-12-molybdic

acid, even if the low diffusion coefficients calculated for these acids are not quite realized. Naturally aggregations between the phosphoric and hexa-isopoly-acids in other stoichiometric ratios can be imagined, for example, in the ratio 2 : 3. The composition thereby conceived for the anhydrous acid $P_2O_5 \cdot 18WO_3$ would correspond to the well-known 9-tungstates, *e.g.*, $P_2O_5 \cdot 18WO_3 \cdot 42H_2O$. These would accordingly be regarded as dinuclear compounds. In the case of vanadic acid, it is worthy of note that it is not one of the stable polyvanadic acids which unites with phosphoric acid to form a complex, but the unstable *octovanadic acid*, which is thereby stabilized. Just as the latter is to be recognized in particular by its characteristic colour, so are the dark-red so-called *purpureo-phosphovanadates*. In these the $P_2O_5 : V_2O_5$ ratio, in spite of similar colour and like chemical behaviour, may be very different, but can always be referred to a simple stoichiometric ratio between phosphoric acid and octovanadic acid. The ratios 1 : 1, 1 : 3, 2 : 1 and 2 : 3 have been observed.

It is not always possible with the heteropolymolybdates and heteropolytungstates to find a simple stoichiometric ratio between the hexa-isopoly-acid and the non-metal acid. Already in the case of silico-10-tungstic acid, for example, the ratio $SiO_2 : 6WO_3 = 6 : 10$ must be assumed. The numerical ratios appear even less likely for the 2 : 21- and 2 : 17-acids, among others, if it is desired to refer them to a hexa-isopoly-acid. More reasonable ratios result if not only a hexa- but also a tri-isopoly-acid can act as the structural unit, which, in accordance with JANDER's considerations concerning the transient existence of a trimolybdic acid (pp. 191, 206), lies completely within the bounds of possibility. But in any case the conditions of formation of these acids and their salts must be more precisely known than has so far been the case, especially the hydrogen-ion concentrations required in their preparation, if even only moderately convincing views concerning their formation are to be expressed. But in these cases, X-ray investigations as well as obvious genetic relationships between isopoly- and heteropoly-acids are lacking. Only the preparative side has been thoroughly studied. In conclusion, it may once again be pointed out that the cause of the difference between silicotungstic and tungstosilicic acids and between analogous "isomeric" acids is even now still unknown.

7. Retrospective Survey of the Methods applied to the Investigation of Isopoly- and Heteropoly-acids

Although many individual questions still remain open, it can finally be affirmed with satisfaction that both of the different methods of investigation, the structural-chemical and the colloid-chemical — as JANDER's researches may be impersonally described — lead in the end to conclusions which in all essential points can be brought into harmony with one another.

With this one might be satisfied were it not for occasional utterances asserting the contrary¹⁶⁸. The reason for such misunderstandings is to be sought in the different approaches which, generally speaking, apply to structural-chemical and colloid-chemical research methods. But because both methods must be combined, not only here but also in other cases, it would be profitable to re-examine the fundamental viewpoints of the various investigators who have been active in the field of isopoly- and heteropoly-acids, in order to achieve a full understanding of all the observations.

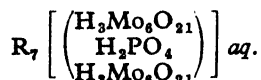
From the outset, structural-chemical investigations place the structure of the compound or of the ion present in solution in the foreground. The only structural-chemical principle which is applicable in inorganic chemistry is WERNER's co-ordination theory. It is consequently only natural that the attempt has also been made to utilize it with respect to the isopoly- and heteropoly-acids. The reason for commencing here with the heteropoly-acids has already been discussed. One structure for the heteropoly-acid anions, which is conceivable on the basis of WERNER's theory, has been put forward with all reserve as a working hypothesis by MIOLATI¹⁶⁹, who had studied with WERNER in Zürich. The observant reader senses that MIOLATI, in publishing this hypothesis, departs only unwillingly from his reserve, since he was clear concerning the uncertainty of the experimental basis. It is however significant that MIOLATI never again intervened later in the discussion about the structure of the heteropoly-acids. MIOLATI's hypothesis was taken up on two sides, by COPAUX and by ROSENHEIM. COPAUX satisfied himself in the main by employing it for the presentation of his results. Being crystallographically interested, it suited him, evidently on account of the spatial picture of the structure with which crystallographers could feel at home. ROSENHEIM went further. He extended MIOLATI's hypothesis to a "theory", in which he simultaneously attempted to broaden the experimental basis and adduce proofs for his and MIOLATI's ideas. In this he availed himself freely in the main of the same preparative and analytical aids as the older experimental investigators in this field. This experimental attitude of ROSENHEIM is to be understood from his schooling, which he had received from FRIEDHEIM. But his theoretical attitude is also to be understood in terms of his career. With FRIEDHEIM, he became aware of the worthlessness of the formulae for inorganic complex compounds made according to the pattern of organic structural formulae, to which FRIEDHEIM adhered. On the other hand, it was a sign of the times that, in consequence of the extraordinary success of structural chemistry in the field of organic chemistry, the determination of a structure or at least a structural principle appeared as one of the highest aims in chemistry. WERNER's ideas here pointed

¹⁶⁸ For example, H. J. EMELÉUS and J. S. ANDERSON in *Modern Aspects of Inorganic Chemistry* (Routledge, 1938). In contradistinction to the authors, JANDER represents the viewpoint adopted here that no fundamental differences exist: p. 183, footnote 2.

¹⁶⁹ A. MIOLATI and R. PIZZIGHELLI, *J. prakt. Chem.*, 1908, [ii], 77, 456.

to new paths in inorganic chemistry. What was more natural than that ROSENHEIM and other investigators of his time should avail themselves of them, even if the experimental basis for their application was in part extraordinarily restricted? It was therefore unavoidable that the question of the *structure* of the isopoly- and heteropoly-acids was next pushed into the foreground, although chemical methods were not available by which the structure could have been determined in something like the manner of structural research in organic chemistry.

This complete lack of chemical methods for determining the structure was felt by JANDER, who had become familiar with the problems of the isopoly- and heteropoly-acids in ROSENHEIM's laboratory. He made his acquaintance with the colloid-chemical way of thinking in ZSIGMONDY's institute. The two viewpoints are so very different, that colloid chemists and structural chemists have frequently not understood one another, but have talked at cross-purposes. Colloid chemistry concerns itself with very unstable forms, namely sols and gels, and studies their formation and disintegration. Often enough, colloids will pass through various states as intermediate stages in the attainment of a stable state of equilibrium. Precisely in the case of the isopoly-acids, the gelatinous state is frequently characteristic for the hydrated oxide precipitated at the iso-electric point. It thus readily suggested itself to JANDER to commence with the isopoly-acids and not the heteropoly-acids, and to enquire into what happens in solution before the isopoly-acids are precipitated, that is, to follow the aggregation processes. In this, he opened up a new experimental path which must appeal to every chemist who is not satisfied with investigating a ready-made substance but also wants to know how it originated. But because the conditions of formation, otherwise than in the planned synthesis of an organic compound, permit no conclusions to be drawn concerning the structure in this case, to the extreme structural chemist such a method of investigation must appear as the wrong one, since it could never lead to its "object", that is, the structural formula. But JANDER did not consciously set out to determine structures. Being no more impressed by the development of organic structural chemistry than were ROSENHEIM and his colleagues, the practice of thinking along structural-chemical lines did not appeal to him. How little of a "structural chemist" he was in reality follows from the formulation he once gave¹⁶⁰ for the salts of phospho-12-molybdic acid, namely



In this expression, one is reminded of the formulae which KOLBE gave for the derivatives of benzene in the seventies, to whom structural-chemical thinking similarly made no appeal.

Neither the structural chemist nor the colloid chemist was able on his

¹⁶⁰ G. JANDER and H. WITZMANN, *Z. anorg. Chem.*, 1933, **215**, 317.

own to grasp the problem of the isopoly- and heteropoly-acids completely, for each, from a different aspect, saw only a part of the whole problem. But, for the experimental *chemist*, the two aspects have a different value. After mastering the preparative and analytical work, the structural chemist is completely at a loss and must satisfy himself with speculations which cannot be proved as long as he is not helped out by the physicist with his completely non-chemical method of X-ray analysis. The colloid chemist, on the other hand, can attain the goal he has set himself by a skilled combination of the most varied chemical and physical methods, and thereby solve the problem from the angle from which he sees it. The isopoly- and heteropoly-acids, when an unbiased survey of the results of all the investigations to which they have been subjected is made, provide a very good example of how different kinds of thinking and research can contribute to the solving of a problem, even when their aims are not identical. It is necessary only to combine them in an intelligent manner.

8. Metaphosphates

Isopoly-acid anions of a kind differing from those of the molybdic, tungstic and vanadic acids are found in the *metaphosphates*. Their existence depends on the fact that phosphorus strives to assume the co-ordination number 4 in the place of 3, so that the unknown monomeric metaphosphate ion PO_3' is not capable of existence, but polymerizes. The polymerization can take place in various ways, as is shown by the existence of different metaphosphates, which also form solutions that can be distinguished. But the relationships involved are so complicated, that it is still not possible to speak of an explanation according to the structural-chemical viewpoint. Even the molecular weights of anions are not in a single instance known with complete certainty, although in some cases they can be given with a fairly high degree of probability. Investigations are rendered more difficult by a number of facts, namely that many of these metaphosphates, even under apparently identical conditions, are not always obtained with the same properties, that the sodium and potassium salts behave differently, and that the anions in solution can undergo changes with time and do not always with certainty remain unchanged in reactions involving precipitation. An impressive picture of the certainty or uncertainty of the conclusions drawn from experiment, with respect to both the reproducibility of the experiments and the partly contradictory results of different investigators, is furnished in a monograph by KARBE and JANDER¹⁰¹, which is referred to on account of the details. Only a few especially thoroughly investigated examples will be selected here, examples in which the question of the molecular weights of the metaphosphate ions has been clarified.

¹⁰¹ K. KARBE and G. JANDER, *Kolloid-Beihefte*, 1942, 54, 1—146. A detailed report of the literature is given.

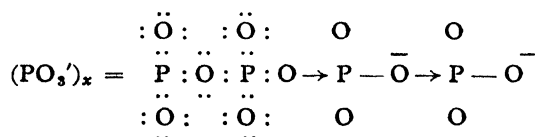
(i) GRAHAM's Salt

The metaphosphate discovered as early as 1834 by T. GRAHAM and named after him is best prepared by prolonged heating of monosodium orthophosphate $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ to above 500° , as GRAHAM himself has indicated. It is also produced in the beads formed on heating microcosmic salt $\text{NaNH}_4\text{HPO}_4$, and is consequently the best known metaphosphate. The latter preparation is less suitable for precise investigations, since small quantities of ammonia are obstinately retained. Commercial "sodium metaphosphate" is a glassy mass which is hygroscopic, but in the compact state dissolves in cold water only slowly, albeit copiously in the end. In warm water it dissolves readily. The solutions exhibit the known metaphosphate reactions. A white flocculent precipitate with the composition AgPO_3 is formed with silver nitrate (and precipitates of similar appearance with Pb^{++} , Hg^{++} , Sr^{++} and Ba^{++}), solutions of albumin are coagulated, and, what is less generally known, gelatinous and oily precipitates are formed with Cu^{++} , Fe^{++} , Mn^{++} , Ni^{++} and Ca^{++} . Zn^{++} gives no precipitate with freshly prepared solutions, but does with an aged solution. With excess of metaphosphate, the precipitates formed with Mg^{++} , Ca^{++} , Ba^{++} , Ag^+ and possibly some other ions are soluble in consequence of the formation of complex salts. Upon this depends the great practical significance of metaphosphates in the technique which makes use of them for the softening of water and which has resulted in numerous publications. Since, however, the latter are for the most part written entirely from the technical standpoint, they have on the whole contributed little to the clarification of the structural relationships of the metaphosphates.

The precipitation of albumin indicates that in solutions of GRAHAM's salt a polymeric metaphosphate ion $(\text{PO}_3')_x$ occurs. Usually, particularly in the technical papers, an aggregation of six PO_3' ions is assumed by virtue of a supposition of T. FLEITMANN dating back to the year 1849, which he himself did not consider to be supported with certainty by experiment. Accordingly the term *hexametaphosphate* is used for GRAHAM's salt. However, as was first shown unquestionably by the careful investigations of G. JANDER and K. KARBE almost 100 years later, this is certainly not correct. Above all, the ion of GRAHAM's salt has no definite molecular weight, but a mean molecular weight which is dependent upon the degree of heating. By long continual heating at well-defined temperatures, melts can be prepared in which the temperature-dependent equilibrium between the metaphosphates aggregated to varying degrees has been attained. By skilled cooling — pouring the melt into well-cooled carbon tetrachloride — this equilibrium is frozen and solutions of the powdered melt investigated. The dialysis procedure of H. BRINTZINGER (p. 202), improved by G. JANDER and H. SPANDAU, has served as method. Since, after a slight fall during the first hours, the dialysis coefficient remains practically constant for several weeks, the experi-

mental results are not falsified by a change in the mean molecular weight through aging. From these experiments, a dependence of the mean molecular weight on the equilibrium temperature of the melt is readily obtained. The dialysis coefficient slowly sinks as the temperature of heating is increased to 1160°, and then rises rapidly above 1200°. Accordingly higher polymers are formed in increasing degree to about 1200°, these rapidly depolymerizing on further increase of temperature. An exact calculation of the degree of polymerization from the dialysis coefficient is not possible on account of the lack of a similar ion which might serve for comparison. With certain though by no means exactly valid assumptions, KARBE and JANDER calculate an estimated degree of polymerization of 88 for the most and 24 for the least highly polymerized GRAHAM's salt. The fact that the degree of polymerization in the melt first increases and then decreases with increasing temperature has, as pointed out by KARBE and JANDER, an analogy in the behaviour of sulphur.

The varying degree of polymerization of the PO_3' ion finds an illuminating structural explanation in the chain structure suggested by WILSON¹⁶²:



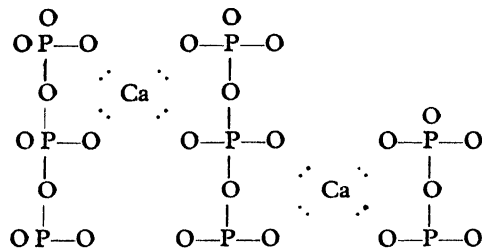
The lone electron pair on the oxygen of one PO_3' ion is thereby inserted into the gap in the octet of a second PO_3' ion. The polymerization of the ions takes place here according to the same principle as occurs with the metasilicate ion SiO_3'' when it forms chains as in diopside, or with the electroneutral molecule SO_3 in its threadlike modification resembling asbestos. That for the metaphosphate ion no threadlike structure arises, depends perhaps on the fact that a chain with branching is possible, in addition to linear chains as shown by the foregoing formula. That would also explain why, as a mixture of straight and branched chains, GRAHAM's salt does not crystallize.

The formation of soluble complex salts can also be explained as inner-complex-formation without difficulty by the use of chain formulae, be these linear or branched. The divalent metal links two chains by ionic bonding and simultaneously links itself by complex-formation to an oxygen atom from each chain. In this, the difference between ionic bonds and complex bonds may at the same time disappear, whereupon each becomes an electron-pair bond (cf. pp. 141—142):

¹⁶² J. A. WILSON, *J. Am. Leather Chemists' Assoc.*, 1937, **32**, 113. The objection brought forward by H. RUDY and H. SCHLOESSER (*Ber.*, 1940, **73**, 490) against this formula appears not to be valid, as KARBE and JANDER (*op. cit.*, p.96) have already emphasized. A chain structure for metaphosphoric acid in GRAHAM's salt, namely

$(\text{HO})_2\text{P}-\overset{\text{OH}}{\underset{\text{O}}{\text{O}}}-\text{P}-\overset{\text{OH}}{\underset{\text{O}}{\text{O}}}-\dots-\text{P}(\text{OH})_2$, is likewise assumed by O. SAMUELSON,

Svensk Kem. Tidskr., 1944, **56**, 343.



The inner-complex salt contains the metal in a six-membered ring. The structures outlined here can by no means be regarded as proved, however. In particular, informative investigations concerning the structure of complex salts, as well as the technically very important connections between the mean molecular weight of the isopoly-anions in GRAHAM's salt and their powers of complex-formation, are still lacking. It is still not quite certainly decided whether, in the acid corresponding to GRAHAM's salt, all of the hydrogen ions dissociate equally readily or not, even if the potentiometric titration appears, according to two different authors¹⁶³, to speak unequivocally for the former possibility.

(ii) KURROL's Salts

GRAHAM's salt proper is a polymeric sodium metaphosphate. A corresponding potassium salt with very similar properties can also be prepared, but with greater difficulty. It is never obtained pure because an insoluble salt is always formed in addition, usually as the main product. This is KURROL's potassium salt¹⁶⁴. Conversely KURROL's sodium salt is more difficult to obtain than the potassium salt, although it has been more studied than GRAHAM's potassium salt. It will however suffice to depict the situation for KURROL's potassium salt¹⁶⁵. The formation of this salt from monopotassium orthophosphate KH_2PO_4 begins as low as 170° , but is only completed after heating to $270\text{--}300^\circ$ for several hours with continual stirring of the melt. It is purified by leaching with water. It solidifies from its melts at 838° in plates. As already mentioned, it is practically insoluble in water but dissolves in solutions of GRAHAM's salt to give viscous solutions whose viscosity depends on the degree and a little on the duration of the previous heating of the salt to temperatures below its melting point. The cooled melt of KURROL's salt solidifies as a glass, is water-soluble, and with GRAHAM's salt does not give particularly viscous solutions. Whether there are different modifications of KURROL's potassium salt which, as PASCAL believed, with GRAHAM's salt provide solutions of significantly different viscosity, may not be regarded as certain merely by reason of the experi-

¹⁶³ H. RUDY and H. SCHLOESSER, *Ber.*, 1940, **73**, 484; E. PARTRIDGE, *Dual Service News, Hall Lab., Pittsburgh*, 1937.

¹⁶⁴ G. TAMMANN, *J. prakt. Chem.*, 1892, [ii], **45**, 467.

¹⁶⁵ P. PASCAL, *Bull. soc. chim. France*, 1924, [iv], **35**, 1124.

mental results so far available. Until now it has not been possible to express an opinion regarding the structure possessed by KURROL's salt.

Still more viscous solutions than those formed by KURROL's salt with GRAHAM's salt or with a pyrophosphate are provided by a salt with the composition $KPO_3 \cdot 2NaPO_3$. It can be obtained from KURROL's potassium salt by treatment with two molecules of sodium chloride solution, whereupon the potassium ion goes into solution and the sodium ion into the residue, which swells up considerably; also from KURROL's potassium salt and silver nitrate solution, followed by melting the residue at 300° and decomposing the glassy solidified melt of composition $2KPO_3 \cdot 4AgPO_3 \cdot H_2O$ with $NaCl$, when the double sodium potassium salt is obtained¹⁶⁶. The solutions are most extraordinarily viscous. A 3% solution possesses about the same viscosity as glycerine. Alcohol precipitates the rubber-like salt, which after a short time in the molten state possesses the composition given above. The double salt $NaPO_3 \cdot KPO_3$, which can be similarly prepared, behaves rather less decidedly as a colloid.

The highly viscous solutions permit no determination of the particle size, either by the diffusion method or by determination of the sedimentation equilibrium in the ultra-centrifuge. On dialysis in 0.1-*N* hydrochloric acid, the potassium ion dialyzes, but not the sodium ion. However, the viscosity is already considerably diminished on treatment with the acid. A similar reduction in the viscosity also follows on the addition of dilute (up to 0.3-*M*) sodium thiocyanate solution or of alkali. In solutions treated with thiocyanate, diffusion measurements and determinations of the sedimentation equilibria have yielded a molecular weight dependent on the concentration, being about 140,000 for a 0.5 % solution, and likewise also in solutions treated with very dilute alkali¹⁶⁷. In view of the high viscosity of solutions of organic colloids, this behaviour is interesting but does not permit any further conclusion to be made regarding the structure of the salts than that their isopoly-anions have exceptionally high molecular weights and that they are possibly aggregated with ultra-microscopic salt crystals, as is the case with the soaps.

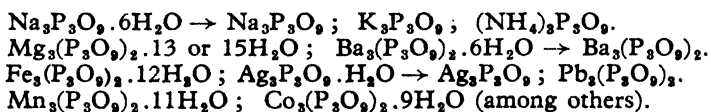
(iii) Trimetaphosphates

The formation of KURROL's potassium salt renders more difficult not only the preparation of GRAHAM's potassium salt, but also that of potassium trimetaphosphate, which in consequence is only to be obtained pure via the easily obtained sodium trimetaphosphate. Among the other trimetaphosphates which are obtainable from it, this is the metaphosphate which has

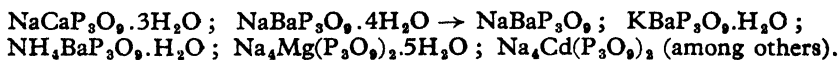
¹⁶⁶ G. TAMMANN, *Z. physik. Chem.*, 1890, **6**, 134.

¹⁶⁷ O. LAMM and H. MALMGREN, *Z. anorg. Chem.*, 1940, **245**, 103. Further investigations: H. MALMGREN and O. LAMM, *ibid.*, 1944, **252**, 256; H. MALMGREN, *Acta Chem. Scand.*, 1948, **2**, 147 (molecular weights up to 1,300,000 found).

been the best studied. These salts must still be termed trimetaphosphates, corresponding to the old naming of T. FLEITMANN¹⁶⁸ dating from the year 1848, since various methods of investigation speak for a trimerization of the metaphosphate ion in them. Sodium trimetaphosphate is formed as a crystalline, not quite pure compound from monosodium orthophosphate NaH_2PO_4 , from microcosmic salt $\text{NaNH}_4\text{HPO}_4$ or from acid sodium pyrophosphate $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$, at about 300° , that is, at an essentially lower temperature than GRAHAM's salt. To purify it, it is dissolved in water, whereupon MADDRELL's salt (see later) stays behind, is then recrystallized and the diluted solution treated with lead nitrate (not lead acetate). This immediately precipitates the insoluble lead salts of other polymetaphosphates, while the lead trimetaphosphate at first remains in solution and crystallizes out only gradually after filtering. The lead trimetaphosphate obtained in this manner is decomposed with sodium sulphate¹⁶⁹. The sodium salt is most conveniently obtained by heating disodium phosphate $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ with ammonium nitrate for 6 hours at 300° . By this method is obtained, in addition to the desired salt, only MADDRELL's salt in variable quantity which, on account of its insolubility, is easily separated. Sodium trimetaphosphate has the composition $\text{NaPO}_3 \cdot 2\text{H}_2\text{O}$, but can also easily be obtained anhydrous. The really great stability of its anion in aqueous solution follows from the possibility of purifying the salt by means of the lead salt, in addition to preparing numerous simple trimetaphosphates and double salts whose formation is very characteristic, *e.g.*, the following compounds, likewise formulated as trimetaphosphates¹⁶⁹:



Double salts:



By way of contrast to the other heavy-metal polymetaphosphates, the heavy-metal trimetaphosphates are on the whole relatively easily soluble, which simplifies the separation from the former, as the forementioned purification by means of the lead salt illustrates.

On account of the stability of the trimetaphosphate ion in solution, experiments to determine the molecular weight can be carried out. The most convincing at the present time may well be the cryoscopic determinations calculated with regard to the DEBYE-HÜCKEL theory of strong electrolytes¹⁷⁰.

¹⁶⁸ T. FLEITMANN and W. HENNEBERG, *Liebigs Ann. Chem.*, 1848, **65**, 307; C. G. LINDBOM, *Ber.*, 1875, **8**, 122; G. TAMMANN, *J. prakt. Chem.*, 1892, [ii], **45**, 427; A. WIESLER, *Z. anorg. Chem.*, 1901, **28**, 201.

¹⁶⁹ G. VON KNORRE, *Z. anorg. Chem.*, 1900, **24**, 381.

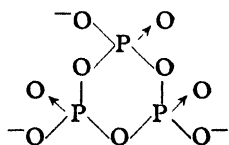
¹⁷⁰ P. NYLÉN, *Z. anorg. Chem.*, 1936, **229**, 32.

These indicate a molecular weight three times that of PO_3' . The same conclusions had already been reached by virtue of the equivalent conductivity¹⁷¹, from which the basicity of the acid radical can be calculated according to the empirical but well founded OSTWALD-WALDEN rule¹⁷². This states that for sufficiently dilute solutions, one equivalent weight to about 32 litres and upwards, the following relationship is valid, namely

$$\lambda_{\infty} - \lambda_v = n_1 \cdot n_2 \cdot c_v.$$

Here λ_v is the conductivity at the dilution v , c is a constant dependent upon the dilution and usually lying between 10 and 11, n_1 is the valency of the cation (here equal to unity) and n_2 the valency of the anion (here sought). For λ_{∞} the value for λ_{1024} can be inserted. Thus, by way of example, for sodium trimetaphosphate it is observed that $\lambda_{1024} = 119.4$ and $\lambda_{32} = 89.4$ reciprocal ohms; hence $\lambda_{1024} - \lambda_{32} = 30 = 1 \cdot n_2 \cdot 10$, so that $n_2 = 3$. Diffusion and dialysis experiments are not in conflict with cryoscopic and conductivity measurements, but they do not permit an exact calculation on account of the difficulty of finding a similar ion of like degree of hydration for service as a reference ion.

One formula which, among others, has been suggested for the trimetaphosphate ion is a ring formula with a non-planar six-membered ring¹⁷³:



The suggestion is based on the results of potentiometric titrations of sodium trimetaphosphate solutions which have been treated with acid or alkali. For these, *one* transition point had been found at p_{H} 6.7, in agreement with potentiometric and conductometric titrations of the freshly prepared acid, for which only *one* potential jump results at p_{H} 6.9¹⁷⁴. According to this, all of the three hydrogen atoms must dissociate with about the same ease, and this is only possible if they are firstly all three bound in the same way and secondly so far removed from one another in space that the negative charge resulting through the dissociation of a hydrogen atom exerts no appreciable electrostatic influence on the dissociation of the other hydrogen atoms. Trimetaphosphoric acid is accordingly a very strong acid whose various dissociation constants lie very close to one another¹⁷⁴. The state of the free acid in solution changes appreciably more rapidly with time than that of its salts.

¹⁷¹ A. WIESLER, *Z. anorg. Chem.*, 1891, **28**, 187; cf. G. TAMMANN, *Z. physik. Chem.*, 1890, **6**, 127.

¹⁷² W. OSTWALD, *Z. physik. Chem.*, 1887, **1**, 75; 1888, **2**, 843; P. WALDEN, *ibid.*, 1887, **1**, 529; 1888, **2**, 49.

¹⁷³ W. D. TREADWELL and F. LEUTWYLER, *Helv. chim. Acta*, 1938, **21**, 1453.

¹⁷⁴ K. KARBE and G. JANDER, *Kolloid-Beihefte*, 1942, **54**, 47. Cf. C. W. DAVIES and C. B. MONK, *J. Chem. Soc.*, 1949, p. 413.

Even if no real structural proof for the ring formula is available, it is nevertheless attractive, especially as it makes the non-occurrence of the formation of inner-complex salts in contradistinction to the chain formula of GRAHAM's salt comprehensible. The structural principle is further transferable to the tetrametaphosphates.

(iv) Tetrametaphosphates

The tetrametaphosphates are still frequently to be found in the literature under the designation dimetaphosphates, corresponding to FLEITMANN's nomenclature of 1849, although since 1903 it has been fairly certain that one is here dealing with tetramerized metaphosphates. In the salts which have been termed tetrametaphosphates by FLEITMANN, on the contrary, the degree of polymerization, not to mention anything about their structure, is still unknown, in spite of a number of more recent investigations. For this reason they will not be discussed here. But this much appears certain, namely that FLEITMANN's tetrametaphosphates are in reality polymerized to an essentially higher degree.

True tetrametaphosphates cannot be obtained directly from acid alkali-metal phosphates. Rather an insoluble heavy-metal salt must first be prepared from phosphoric acid and a heavy-metal oxide or salt of a volatile acid by heating, and this decomposed with a solution of an alkali sulphide in order to obtain the soluble alkali salt. The insoluble alkaline-earth tetrametaphosphates are formed in the same way as the tetrametaphosphates of the heavy metals. Not all the heavy-metal oxides give tetrametaphosphates smoothly in the way described. Cadmium, lead and bismuth yield more highly polymerized metaphosphates which FLEITMANN erroneously took for tetrametaphosphates. Whether the one or the other kind of metaphosphate is formed depends upon the temperature of preparation. If this remains below the melting point of the tetramer, the tetrametaphosphate may be formed, but in other cases the higher polymer. If the melting point of the tetramer is very low, as in the cases of cadmium, lead and bismuth, the tetramer is not observed and the higher polymer only is obtained¹⁷⁵. The most advantageous way of preparing the tetrametaphosphates is probably via the lead salt, for which the conditions under which both it and the higher polymer are formed are well-known¹⁷⁶.

As in the case of the trimetaphosphates, anhydrous salts and salts containing water of crystallization, simple salts and numerous double salts are known among the tetrametaphosphates. The charge on the anion has here likewise been determined by the application of the OSTWALD-WALDEN rule and found to be 4¹⁷⁷; for example, from the sodium salt, which has the values $\lambda_{1024} = 126.2$ and $\lambda_{32} = 85.6$. The transport numbers also

¹⁷⁵ A. GLATZEL, *Dissertation*, Würzburg, 1880.

¹⁷⁶ F. WARSCHAUER, *Z. anorg. Chem.*, 1903, **36**, 158.

¹⁷⁷ F. WARSCHAUER, *Z. anorg. Chem.*, 1903, **36**, 150.

conform to the formula $(\text{PO}_3)_4$ '''''. Recently this result has been confirmed by cryoscopic measurement¹⁷⁸.

At 410°, sodium tetrametaphosphate is converted to a water-insoluble metaphosphate which, at still higher temperatures, changes into the trimetaphosphate and then into GRAHAM'S salt. These salts can be differentiated by their X-ray interference patterns which, however, have not so far been explained¹⁷⁹. On account of the lack of experimental foundations, structural suggestions for the tetrametaphosphate ion have not yet been put forward. The analogy with the trimetaphosphates, set out above as a possibility, does not appear to be supported by any experiment (but cf. the crystal structure of $\text{Al}(\text{PO}_3)_3$ discussed below).

(v) MADDRELL'S Salt

MADDRELL'S salt¹⁸⁰ is formed, usually only in small quantities but sometimes in preponderance, during the preparation of sodium trimetaphosphate. The surest way of obtaining it is by heating sodium nitrate dissolved in a very little water with syrupy phosphoric acid in rather more than the theoretically required quantity to 350° for about 4 hours. It is very slightly thesoluble in water (only about 0.1 g per litre), but is distinguished from the insoluble KURROL'S salt in that the part dissolved in water changes into trimetaphosphate. MADDRELL'S salt does not form double salts. The assumption that it is monomeric, like the formulation as dimetaphosphate, which has also been suggested, remains completely unsupported. In reality, nothing is known concerning the degree of polymerization or the structure of the salt.

A soluble sodium metaphosphate, which is certainly wrongly spoken of as monomeric, has been obtained by PASCAL¹⁸¹ from the polymeric ethyl ester of metaphosphoric acid (from ether and phosphorus pentoxide) and sodium ethylate. Whether it is at all a single substance appears questionable. Like solutions of all the metaphosphates, its solutions precipitate albumin. This speaks for the presence of polymers, as is also indicated by cryoscopic measurement.

For the sake of completion, the *polyphosphates* should also be mentioned. These are formed on heating metaphosphates and pyrophosphates in stoichiometric proportions, e.g., $\text{NaPO}_3 + \text{Na}_4\text{P}_2\text{O}_7 = \text{Na}_5\text{P}_3\text{O}_{10}$. The existence of this tripolyphosphate as an independent compound has been made certain by X-ray studies¹⁸², but its structure has not been determined any more than have those of the other polyphosphates. With the alkaline-earths and heavy metals, the polyphosphates form soluble inner-complex

¹⁷⁸ P. NYLÉN, *Z. anorg. Chem.*, 1936, **229**, 34.

¹⁷⁹ P. BONNEMAN, *Compt. rend.*, 1937, **204**, 865; A. BOULLÉ, *ibid.*, 1938, **206**, 1732.

¹⁸⁰ R. MADDRELL, *Liebigs Ann. Chem.*, 1847, **61**, 63.

¹⁸¹ P. PASCAL, *Compt. rend.*, 1923, **176**, 1398; *Bull. soc. chim. France*, 1923, [iv], **33**, 1613.

¹⁸² K. R. ANDRESS and K. WÜST, *Z. anorg. Chem.*, 1938, **237**, 113; 1939, **241**, 196; H. HUBER and K. R. ANDRESS, *ibid.*, 1939, **243**, 110.

salts like GRAHAM's salt, and consequently also find the same technical application as the latter.

The crystal structure has been elucidated for a single crystallized metaphosphate, namely aluminium metaphosphate $\text{Al}(\text{PO}_3)_3$ ¹⁸³. In the lattice, four metaphosphate ions are linked together to form a P_4O_{12} ring in which four PO_4 tetrahedra make contact by their corners. The eight oxygen atoms not forming part of the ring belong to eight different AlO_6 octahedra which surround the cyclic P_4O_{12} group. The distance between P and O is 1.5 Å and that between Al and O 1.83 Å, so that, notwithstanding, the P_4O_{12} ring stands out in the lattice as a discrete grouping. It is possible that the same ring occurs in the soluble tetrametaphosphates, which are in fact obtained from the insoluble metaphosphates of the heavy metals.

9. Silicic Acid and the Soluble Silicates

When considering the numerous investigations on silicic acid, it is necessary to distinguish between the studies having the proof of existence of certain anions of silicic acid in solutions of the soluble alkali silicates as object, those which are concerned with the state of free silicic acid in solution and those relating to the hydrogels of silicic acid. Although research originally applied itself to gels and most of the observations refer to these, the studies which concern the alkali silicates and the soluble silicic acids and were designed with another object in view will be given first place here, since they deal with the initial stages of hydrogel-formation, that is, to the extent that silicic acid gel is produced by acidifying silicate solutions.

(i) Silicic Acid Anions in Silicate Solutions

In order to learn something about silicate ions in solution, it is best to commence with crystallographically uniform silicates. The melting-point diagram for $\text{Na}_2\text{O} + \text{SiO}_2$ indicates the existence of four sodium silicates: Na_4SiO_4 , m.p. 1083°; $\text{Na}_6\text{Si}_2\text{O}_7$, m.p. 1122°; Na_2SiO_3 , m.p. 1098°; $\text{Na}_2\text{Si}_2\text{O}_5$, m.p. 874°¹⁸⁴. From aqueous solutions, the hydrated sodium metasilicate $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ of melting point 47°¹⁸⁵ and the disilicate $\text{Na}_2\text{Si}_2\text{O}_5 \cdot 9\text{H}_2\text{O}$ ¹⁸⁶ crystallize.

Barium hydroxide precipitates BaSi_2O_5 from a freshly prepared solution of $\text{Na}_2\text{Si}_2\text{O}_5$, a mixture of BaSiO_3 and BaSi_2O_5 from a solution of Na_2SiO_3

¹⁸³ L. C. PAULING and J. SHERMAN, *Z. Krist.*, 1937, **96**, 481.

¹⁸⁴ J. D'ANS and J. LÖFFLER, *Z. anorg. Chem.*, 1930, **191**, 1. Part of the diagram for Na_2SiO_3 and SiO_2 : G. W. MOREY and N. L. BOWEN, *J. Phys. Chem.*, 1924, **28**, 1167.

¹⁸⁵ K. A. VESTERBERG, *Z. anorg. Chem.*, 1914, **88**, 341; *Mitt. VIII int. Kongr. angew. Chem.*, 1912, **2**, 235. On adding alcohol, the hydrates with $2\frac{1}{2}$ and $6\text{H}_2\text{O}$ are also formed, which however are decomposed by water: R. W. HARMAN, *J. Phys. Chem.*, 1927, **31**, 511.

¹⁸⁶ R. W. HARMAN, *J. Phys. Chem.*, 1927, **31**, 511.

and likewise from a solution of Li_4SiO_4 ¹⁸⁷. From these **precipitation reactions**, SCHWARZ concludes that only the ions $\text{Si}_2\text{O}_5''$ and SiO_3'' occur in solution. This conclusion is not necessarily binding if the ions $\text{Si}_2\text{O}_5''$ and SiO_3'' rapidly set up equilibria with the anions of other silicic acids whose barium salts are more soluble. That with dichromate solutions and barium or lead ions only BaCrO_4 or PbCrO_4 , respectively, is obtained may not be regarded as proof against the existence of the $\text{Cr}_2\text{O}_7''$ ion.

But thorough investigations concerning the state of solution of the sodium silicates for various $\text{Na}_2\text{O} : \text{SiO}_2$ mixture ratios also lead to the same result. However, many pieces of investigation leave the question open whether instead of the ion $\text{Si}_2\text{O}_5''$ the ion HSiO_3' is not present, these existing in equilibrium: $2\text{HSiO}_3' \rightleftharpoons \text{Si}_2\text{O}_5'' + \text{H}_2\text{O}$ ¹⁸⁸. Nevertheless, it is now certain that this equilibrium lies far to the right. Measurements of the conductivity, viscosity, vapour pressure and depression of freezing point, electrometric titrations and observations relating to diffusion and the absorption of light are available. Even if, on critical examination, the results of the individual observers do not appear to be absolutely certain, there can however be scarcely any doubt, on account of the variety of the material in support of proof, that the conclusions are in essence correct.

The **equivalent conductivity**¹⁸⁹ of sodium silicate solutions of varying composition manifests in dilute solutions only one break in the curve at the $\text{Na}_2\text{O} : \text{SiO}_2$ ratio 1 : 2, and in concentrated solutions also at the ratios 1 : 1 and 2 : 1¹⁹⁰. For the ratio 2 : 1, however, the discontinuity is apparently so slight, that no conclusions can be drawn from it regarding the existence of SiO_4'''' ions.

From **electrometric titrations**¹⁹¹ for determining the concentration of hydroxyl ions in sodium silicate solutions of varying composition and concentration, it has been possible to derive the hydrolysis constant. For the first dissociation constant of H_2SiO_3 , k_1 has a value of the order of 10^{-9} : for the second, k_2 is about 10^{-13} . In the main, hydrolysis proceeds only as far as the HSiO_3' ion. Whether this forms $\text{Si}_2\text{O}_5''$ with the loss of water cannot, of course, be decided in this way. By combining the degree of hydrolysis with the depression of freezing point, it can be deduced that up to the $\text{Na}_2\text{O} : \text{SiO}_2$ ratio 1 : 2, corresponding to NaHSiO_3 or $\text{Na}_2\text{Si}_2\text{O}_5$, either no colloidal silicic acid or only very little is present. With more SiO_2 , on the other hand, part of it is certainly present as colloidal silicic acid. How

¹⁸⁷ R. SCHWARZ and H. RICHTER, *Ber.*, 1927, **60**, 2269.

¹⁸⁸ The view that NaHSiO_3 is present was first represented by E. JORDIS and E. H. KANTER, *Z. Elektrochem.*, 1902, **8**, 678. Cf. E. JORDIS, *J. prakt. Chem.*, 1908, [iii], **77**, 236; E. JORDIS and W. HENNIS, *ibid.*, p. 260 (also the equilibrium with $\text{Si}_2\text{O}_5''$).

¹⁸⁹ R. W. HARMAN, *J. Phys. Chem.*, 1925, **29**, 1155.

¹⁹⁰ The discontinuity at 1 : 2 had already been observed by F. KOHLRAUSCH, *Ann. Physik*, 1892, [ii], **47**, 756; *Z. physik. Chem.*, 1893, **12**, 773.

¹⁹¹ G. HÄGG, *Z. anorg. Chem.*, 1926, **155**, 21. For k_1 , R. W. HARMAN gives the value 4.2×10^{-10} . The older estimates of it, namely the values $k_1 = 1.6 \times 10^{-10}$ and $k_2 = 0.5 \times 10^{-10}$ apparently deserve little confidence.

far these are subject to changes with time in consequence of aging was not investigated in this instance.

The **diffusibility**¹⁹² for solutions of $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ in varying concentration, these having first been brought to various hydrogen-ion concentrations by the addition of alkali or hydrochloric acid and allowed to age, has been determined by diffusion into electrolyte solutions of the same p_{H} placed on top in layers. The electrolyte employed for the upper layer, KOH, KNO_3 or a mixture of both, was also added to the silicate solution. In very strongly alkaline solution comparable with 3-N KOH, the diffusion coefficient is dependent upon the concentration. In less strongly alkaline solution, it decreases to become constant again between p_{H} 13.6 and p_{H} 10.0. A slight dependence upon the concentration is without theoretical significance. From p_{H} 10.9 onwards, which corresponds to a ratio of H⁺ to Na_2SiO_3 of > 1.5 , the diffusion coefficient decreases and becomes changeable with time. Such solutions are unstable and gradually precipitate hydrated silica.

The two regions of constant diffusibility, with the diffusion coefficients $D_{10,z} = 0.62$ and 0.40 , correspond to two silicate ions of different degrees of aggregation. On account of the unknown degree of hydration of these ions, a calculation of the molecular weight with any sort of precision is not possible, for the rate of diffusion of light ions is strongly dependent on their hydration. Nevertheless, by comparison with the rates of diffusion of orthophosphates, it can be concluded from the ratio of the two numerical values that the ions are related to one another as SiO_3'' ¹⁹³ and $\text{Si}_2\text{O}_5''$, and are in any case not equally highly aggregated, as would be required by the existence of an acid monosilicate ion HSiO_3' .

Light absorption of the same solutions, which for p_{H} 13.6 to 10.9 lies at rather shorter wave-lengths than for $p_{\text{H}} > 14$, is also in harmony with the assumption that the ion occurring in the less strongly alkaline region is more highly aggregated. But the differences are so small that no certain opinion may be based on them alone.

Viscosity measurements¹⁹⁴ point to the existence of colloidal silicic acids at $\text{Na}_2\text{O} : \text{SiO}_2$ ratios $> 1 : 2$, in agreement with observations concerning solutions of Na_2SiO_3 to which more than 1.5 equivalents of acid have been added ($p_{\text{H}} < 10.9$). It is not possible to draw more far-reaching conclusions from these measurements.

In the case of *stannic acid*¹⁹⁵, acidified solutions of alkali stannates become unstable as soon as the p_{H} is less than 11.6. In addition, the p_{H} -dependent equilibrium between SnO_3'' and $\text{Sn}_2\text{O}_5''$ also exists with the stannates. On account of the firm binding of the "water of crystallization" in

¹⁹² G. JANDER and W. HEUKESHOVEN, *Z. anorg. Chem.*, 1931, **201**, 361; G. JANDER and K. F. JAHR, *Kolloid-Beihfte*, 1935, **41**, 48.

¹⁹³ JANDER and HEUKESHOVEN in point of fact specify $[\text{NaSiO}_3 \cdot aq]'$ as ion, but according to the theory of strong electrolytes it is improbable that sodium should remain bound to the silicate ion in solution.

¹⁹⁴ V. R. MAIN, *J. Phys. Chem.*, 1926, **30**, 535.

¹⁹⁵ G. JANDER, F. BUSCH and T. ADEN, *Z. anorg. Chem.*, 1929, **177**, 345.

$\text{Na}_2\text{SnO}_3 \cdot 3\text{H}_2\text{O}$, which cannot be removed without hydrolysis of the salt, a hydration of the SnO_3'' ion to $\text{Sn}(\text{OH})_6''$ — in analogy to SnCl_6'' — is to be assumed for the monostannates¹⁹⁶. Whether the SiO_3'' ion is hydrated in the same way, must for the moment remain undecided.

(ii) Silicic Acid in Solution

For the preparation of free silicic acid, the following procedures come into consideration:

- acidification of solutions of alkali silicates¹⁹⁷;
- hydrolysis of silicon halides, especially silicon tetrachloride¹⁹⁸;
- hydrolysis of esters of silicic acid¹⁹⁹;
- hydrolysis of silicon disulphide²⁰⁰.

The following methods may serve as a means of studying the state of silicic acid in solution:

- determination of the molecular weight by freezing-point depression;
- behaviour on diffusion and dialysis;
- precipitation with albumin, which occurs only in the case of colloidal hydrated silica of higher molecular weight;
- light absorption.

Silicic acid from alkali silicates. — In the preparation of silicic acid from alkali silicate solutions, the presence of the alkali salts, which arise at the same time, makes itself disturbingly noticeable in the study of the dissolved state. During prolonged dialysis for their removal, changes of state in solution can occur. It is in fact observed that shortly after acidification silicic acid diffuses through the membrane of the dialyzer²⁰¹, which it does not do at a later stage. At the beginning, therefore, it must be present at least in part as dispersed molecules, from which it is later converted into a more coarsely dispersed colloidal state. More precise data concerning the molecularly dispersed state²⁰² cannot however be obtained, since the alkali salt present renders an evaluation of freezing-point measurements more difficult, and since a change of molecular weight with time must be reckoned with. Only after the hydrogen-ion concentration had been approximately determined for the silicic acid solutions prepared from silicon tetrachloride, in which the molecularly dispersed state is at its stablest, was it possible to overcome these difficulties. During the preparation, the corresponding p_{H} was continuously maintained by buffering²⁰³.

¹⁹⁶ Regarding $\text{Sb}(\text{OH})_6'$ in antimonates, see Chapter VIII, 3, and Chapter XI, 3, (iii).

¹⁹⁷ T. GRAHAM, *Compt. rend.*, 1864, **59**, 174; *Ann. chim. phys.*, 1864, [iv], **3**, 127.

¹⁹⁸ E. EBLER and M. FELLNER, *Ber.*, 1911, **44**, 1915.

¹⁹⁹ E. GRIMAUX, *Compt. rend.*, 1883, **98**, 1485; *Ber.*, 1884, **Referate 17**, 345.

²⁰⁰ J. J. BERZELIUS, *Lehrbuch der Chemie I*, p. 130 (2nd Ed., 1832); E. FREMY, *Ann. chim. phys.*, 1853, [iii], **38**, 312.

²⁰¹ E. JORDIS, *Z. Elektrochem.*, 1902, **8**, 678; F. MYLIUS and E. GROSCHUFF, *Ber.*, 1906, **39**, 118.

²⁰² MYLIUS F. and E. GROSCHUFF, *Ber.*, 1906, **39**, 116.

²⁰³ H. KRAUT, *Ber.*, 1931, **64**, 1709.

A solution of $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ was treated at 0° with hydrogen chloride and varying quantities of acetic acid, in order to obtain a 1% solution of SiO_2 . At the optimum p_{H} for stability, 3.2 for this dilution, the molecular weight was found to be 60, thus corresponding to a monosilicic acid $\text{SiO}_2 = 60$, $\text{H}_2\text{SiO}_3 = 78$). At p_{H} 2.5 the observed molecular weight was near to that of a disilicic acid at 120. Approximately the same molecular weights at the same p_{H} values were determined for silicic acid solutions which had been prepared by hydrolysis of silicon tetrachloride with solutions of sodium acetate, and which had the same compositions as the solutions prepared from alkali silicate solutions. The influence of the hydrogen-ion concentration on the dissolved state of silicic acid is thus evident. Yet in its origin there is another factor, as is seen on substituting acetic acid by other organic acids²⁰⁴.

In the course of time the molecular weight increases. At p_{H} 3.2 it doubles itself in less than 5 days, while at the values 2.8 and 3.3 it is more than trebled in one day. The rate of aggregation is subject to no inconsiderable extent to catalytic influences, the causes of which are still unexplained. Thus in vessels coated with paraffin wax it is higher than in ordinary glass vessels. The addition of aged solutions also increases it, so that in aging one is dealing with an autocatalytic reaction. The aged solution precipitates albumin, whereas the original solution does not²⁰⁵.

The light absorption of a fresh solution of silicic acid prepared from sodium silicate and perchloric acid, which still contains the sodium perchlorate formed at the same time, shows an absorption displaced somewhat (about 20—30 $\text{m}\mu$) towards shorter wave-lengths relative to the alkali silicate solutions²⁰⁶. From this, JANDER concludes the existence of a special pseudo-monosilicic acid differing from the mono- and disilicic acids present in alkaline solution. Such a supposition appears to be superfluous, however, since a certain difference between the absorption of the SiO_3'' or $\text{Si}_2\text{O}_6''$ ion and that of the undissociated acid H_2SiO_3 is not in the least surprising.

Silicic acid from silicon tetrachloride. — The preparation of silicic acid by hydrolysis of silicon tetrachloride offers the advantage of yielding, after the removal of the hydrochloric acid formed simultaneously, a practically pure solution of silicic acid, in which a determination of the molecular weight is less open to objection than in the presence of salts which always cause the major part of the freezing-point depression. The removal of the hydrogen chloride can be effected without bringing electrolytes into solution by the use of precipitated silver oxide²⁰⁷. However, this must be added carefully in small portions immediately as the hydrolysis advances, for, as already mentioned, silicic acid is relatively stable in solution only within

²⁰⁴ H. KRAUT, *op. cit.*, p. 1711.

²⁰⁵ F. MYLIUS and E. GROSCHEFF, *loc. cit.*

²⁰⁶ G. JANDER and W. HEUKESHOVEN, *Z. anorg. Chem.*, 1931, **201**, 361.

²⁰⁷ R. WILLSTÄTTER, H. KRAUT and K. LOBINGER, *Ber.*, 1928, **61**, 2280; 1929, **62**, 2027.

a narrow p_H region, which, in these self-same experiments, was first recognized as lying in the neighbourhood of 3. At the beginning the molecular weight of 62 corresponds to monosilicic acid, and only doubles itself in $2\frac{1}{2}$ days. At p_H 5 it becomes four times as great in as many hours. The ease of dialysis proceeds parallel to the molecular weight. Mono- and disilicic acids do not precipitate albumin, nor, in general, with the middle molecular weights of 200—300 (tri- to tetrasilicic acid) does the precipitation of albumin set in. Disilicic acid changes more rapidly than monosilicic acid. The behaviour of silicic acid obtained from silicon tetrachloride is thus exactly the same as that prepared from alkali silicates.

Silicic acid solutions prepared from silicic esters have not been investigated. Since hydrogen ions are necessary to catalyze the hydrolysis of the esters, they would not be obtained completely free from electrolyte. The hydrogen ions required for the hydrolysis could further influence the aggregation of the silicic acid. It is not probable that silicic acid solutions obtained in this way would differ from those obtained from alkali silicates and silicon halides.

In contrast, such a difference appears to be completely possible for silicic acid prepared from silicon disulphide, which possesses a fibrous structure. However, an investigation of its nature has not yet been carried out.

(iii) Hydrogels of Silicic Acid

The silicic acid which is precipitated on the hydrolysis of suitable silicon compounds and on acidifying silicate solutions is a hydrate of silica. It is not a compound of constant composition, but a gel with a changing water content. The question whether, in the last resort, compounds defined by a stoichiometric $\text{SiO}_2 : \text{H}_2\text{O}$ ratio might be present, and which could be obtained on careful dehydration of the gels, has been much studied. For a long time it was believed, by reason of the careful labours of VAN BEMMELEN²⁰⁸, that no stoichiometric compounds between silica and water existed. Later, however, proof for such was obtained in individual cases, but here it nevertheless appears that definite silica hydrates have sometimes been prematurely decided upon. The preparation of defined silicic acids is connected with the use of certain crystallized water-soluble silicates or other silicon compounds, as well as painstakingly keeping to definite conditions during both the precipitation and drying of the silicic acid. In no case has a naturally occurring, water-insoluble silicate yielded the corresponding silicic acid on being decomposed by acids. All statements to the contrary²⁰⁹ have finally turned out to be erroneous²¹⁰. That VAN BEMMELEN

²⁰⁸ J. M. VAN BEMMELEN, *Z. anorg. Chem.*, 1897, **13**, 233; 1908, **59**, 225; 1909, **62**, 1; R. ZSIGMONDY, *ibid.*, 1911, **71**, 356.

²⁰⁹ E.g., G. TSCHERMAK, *Z. physik. Chem.*, 1905, **53**, 349.

²¹⁰ R. SCHWARZ and H. RICHTER, *Ber.*, 1927, **60**, 2263.

did not find any stoichiometrically composed silicic acids, but found rather in his dehydration experiments a continual decrease in the water content of his gels, is mainly to be attributed to his commencing his preparations with a water-glass which was chemically not exactly defined, and further to his employment of isothermal dehydration by decreasing the pressure in stages as the only procedure for drying.

On decomposing the crystalline sodium silicates Na_2SiO_3 and $\text{Na}_2\text{Si}_2\text{O}_5$ by carefully neutralizing with sulphuric acid in the cold, hydrogels are obtained, which on dehydration under the same conditions behave similarly²¹¹. In the isothermal dehydration over sulphuric acid of varying concentration and phosphorus pentoxide in a vacuum desiccator, as well as in the removal of water by acetone according to the procedure of WILLSTÄTTER and KRAUT²¹², followed by treatment with petroleum ether and storage in a vacuum desiccator, a distinct halt is to be observed at 13 % H_2O , corresponding to $2\text{SiO}_2 \cdot \text{H}_2\text{O}$, this admittedly after the first especially rapid loss of water by the gel has already terminated at 17%, that is, not at a definite hydrate. The disilicic acid thus prepared exhibits X-ray interferences which, however, have not been explained. It is nevertheless crystalline. It has nothing to do directly with the molecularly dispersed disilicic acid in silicic acid solutions, since the hydrate obtained in the gel has with certainty a high molecular weight, being $[\text{H}_2\text{Si}_2\text{O}_5]_x$ or perhaps, according to WILLSTÄTTER, $[\text{H}_2\text{SiO}_3]_n \cdot (n - 1)\text{H}_2\text{O}$ ²¹³. In any case, this acid is stable over a large vapour-pressure range, At $+2^\circ$, an unstable amorphous metasilicic acid $[\text{H}_2\text{SiO}_3]_x$ can also be obtained from Na_2SiO_3 , whose dehydration according to various procedures must likewise be undertaken at 2° ²¹⁴. Dehydration of the hydrogels by liquid ammonia²¹⁵ likewise gives hydrates of stoichiometric composition, of which that obtained from $\text{Na}_2\text{Si}_2\text{O}_5$ again corresponds to the formula $\text{H}_2\text{Si}_2\text{O}_5$. By contrast, the gel obtained from Na_2SiO_3 yields the hydrate $3\text{SiO}_2 \cdot \text{H}_2\text{O}$.

The gels obtained by decomposition of silicon tetrachloride form a less clear picture. It must remain undecided whether they really all exist, especially since X-ray exposures have not been made. Dehydration with liquid ammonia yields no stoichiometric hydrate. On the other hand, dehydration of the gel prepared from SiCl_4 and ice-water accomplished at 2° appears to lead to the same unstable metasilicic acid $[\text{H}_2\text{SiO}_3]_x$ that is observed in the decomposition of sodium metasilicate²¹⁶. Other hydrates have been obtained from hydrogels prepared from SiCl_4 and concentrated hydrochloric acid followed by ammoniacal ammonium chloride and dried according to

²¹¹ R. SCHWARZ and E. MENNER, *Ber.*, 1924, **57**, 1477 (including a report of the older literature); 1925, **58**, 73; R. SCHWARZ and H. RICHTER, *ibid.*, 1927, **60**, 1111; 2263; 1928, **62**, 31.

²¹² R. WILLSTÄTTER and H. KRAUT, *Ber.*, 1924, **57**, 1082.

²¹³ R. WILLSTÄTTER, H. KRAUT and K. LOBINGER, *Ber.*, 1928, **61**, 2290.

²¹⁴ R. SCHWARZ and H. RICHTER, *Ber.*, 1927, **60**, 1114.

²¹⁵ W. BILTZ, *Z. Elektrochem.*, 1927, **33**, 491; W. BILTZ and E. RAHLFS, *Z. anorg. Chem.*, 1928, **172**, 273; R. SCHWARZ and H. RICHTER, *Ber.*, 1929, **62**, 31.

²¹⁶ R. SCHWARZ and H. RICHTER, *Ber.*, 1929, **62**, 31.

the acetone and petroleum-ether procedure²¹⁷. For these the compositions $3\text{SiO}_2 \cdot 2\text{H}_2\text{O}$, $2\text{SiO}_2 \cdot \text{H}_2\text{O}$ and $3\text{SiO}_2 \cdot \text{H}_2\text{O}$ have been determined.

The necessity of regarding these hydrates with caution is shown by the experiments which have been carried out on the silica hydrates obtained from tetraethyl silicate by very slow hydrolysis²¹⁸. In these, the breaks in the dehydration curves are apparently simulated owing to incomplete attainment of equilibrium between the hydrogel and the vapour phase²¹⁹. A metasilicic acid $(\text{H}_2\text{SiO}_3)_x$ is *perhaps* the only definite hydrate which can be obtained in this way²²⁰.

The experiments in which silicon tetrachloride is hydrolyzed by triphenylcarbinol in absolute ether are worthy of mention. It is certain that no orthosilicic acid H_4SiO_4 is thereby formed, and apparently also no metasilicic acid, although the composition of the resulting hydrate is close to that of the formula H_2SiO_3 ²²¹.

The investigation of silicic acid and the water-soluble silicates leads in a direction in which the co-ordination theory verified for salts finds no successful application. Nor has it led to the structures of the water-insoluble silicates, which at least permit the utilization of the concept of the co-ordination theory. The problems which arise thereby cannot be mastered with simple structural conceptions. They are not limited to silica hydrate, but appear in all of the partly amorphous, partly crystalline hydrates of oxides, like those which aluminium, trivalent iron, tin, titanium and also many other elements are able to form.

In the heteropoly- and isopoly-acids, the limit of serviceability of WERNER'S co-ordination theory comes clearly into the picture. Not that the co-ordination concept as such breaks down, but that the possibilities of co-ordination are so many that it is no longer possible to assign without arbitrariness a particular multinuclear co-ordination formula to a particular substance. This arbitrariness can be excluded only where there are crystalline compounds whose structures can be investigated by X-rays. In the silicic acid solutions and gels, where this is not possible, resort must be made to quite different methods of research. Passing from silicic acid to the silicates, X-ray analysis is the only means of bringing a useful systematic order into this extensive field of almost completely insoluble crystalline compounds which do not melt unchanged. Although the co-ordination idea also predominates here, the chemistry of silicates is consequently better discussed under crystal chemistry than in connection with the classical co-ordination theory.

²¹⁷ R. WILLSTÄTTER, H. KRAUT and K. LOBINGER, *Ber.*, 1925, **58**, 2462; 1928, **61**, 2290.

²¹⁸ P. A. THIESSEN and O. KOERNER, *Z. anorg. Chem.*, 1929, **182**, 343.

²¹⁹ H. B. WEISER, W. O. MILLIGAN and W. J. COPPOC, *J. Phys. Chem.*, 1939, **43**, 1109.

²²⁰ Likewise definite hydrates of tin dioxide do not exist: H. B. WEISER and W. O. MILLIGAN, *J. Phys. Chem.*, 1932, **36**, 3030.

²²¹ W. DILTNEY and E. HÖLTERHOFF, *Ber.*, 1929, **62**, 24.

10. Isopoly-bases

The same lines of research and experimental technique as have been employed for silicic acid and the soluble silicates lead to the *isopoly-bases*²²², which form numerous, weakly basic hydroxides. With these, oxygen-containing cations of higher molecular weight can be formed from simpler cations in the same way as the anions of higher molecular weight among the isopoly-acids are formed by the linking up of simpler anions. With the isopoly-bases, however, the relationships are less simple, and have not been so thoroughly studied. Nevertheless, the co-ordination theory can again serve here as a preliminary guide. Even if it is not able to answer the questions which arise in a constructive manner, it does provide a picture of the structural possibilities of linking up simple cations to form cations of higher molecular weight. Deciding between these is the task of a research which must develop in a classical sense by way of the formal application of a structural theory.

The transference of the co-ordination theory in conjunction with the ionic theory to the isopoly-bases appears at first sight to be less simple, because, in the case of the isopoly-acids, one can operate directly with the usual formulae for the oxygen-containing anions without considering their hydration. With the isopoly-bases, however, this is not possible, since the bare elementary cations cannot combine with one another. The co-ordination theory here supplies its first assistance. The aquo-cations must be made the starting-point of the considerations. In this way, the hydrolysis of a salt of a weak base, which finally leads via a gelatinous hydrated oxide either to a crystalline hydroxide or to the oxide plus water, can be represented in a manner similar to the hydrolysis of a salt of a very weak acid like silicic or stannic acid. The concept of the hydrolysis of salts of weak bases will be dealt with in detail in Chapter XI with the discussion on the problem of the strengths of bases and acids.

Weakly basic hydroxides are found only in the cases of polyvalent metals. Of these, however, by no means all are able to form isopoly-bases. Thus neither in the only weakly hydrolyzed magnesium solutions²²³, nor in the more strongly hydrolyzed zinc²²⁴ and uranyl solutions are cations of high molecular weight formed. This has been shown for broad p_H regions from strongly acid solutions to the points where the solubility products of the hydroxides are reached, partly by diffusion experiments²²⁵ and partly by potentiometric experiments²²⁶. On the other hand, it was possible to demonstrate the presence of such cations in solutions of beryllium²²⁷, aluminium^{227, 228},

²²² Review: G. JANDER and K. F. JAHR, *Kolloid-Beihefte*, 1936, **43**, 295.

²²³ W. HEUKESHOVEN and A. WINKEL, *Z. anorg. Chem.*, 1933, **213**, 1.

²²⁴ J. K. GJALDBAER, *Z. anorg. Chem.*, 1925, **144**, 145; 269.

²²⁵ G. JANDER and K. F. JAHR, *Kolloid-Beihefte*, 1936, **43**, 299—300.

²²⁶ M. PRYTZ, *Z. anorg. Chem.*, 1931, **200**, 133.

²²⁷ G. JANDER and W. SCHEELE, *Z. anorg. Chem.*, 1932, **206**, 241.

²²⁸ G. JANDER and A. WINKEL, *Z. anorg. Chem.*, 1931, **200**, 257.

ferric²²⁹ and chromic²³⁰ salts. It is certain that the salts of other weak bases behave likewise. The quantity of cations of high molecular weight has, as with the isopoly-acid anions, in this way proved to be strongly dependent on the hydrogen-ion concentration, with the difference that, for the isopoly-bases, no p_H regions are found in which one particular isopoly-base cation is as good as exclusively capable of existence. A further difference exists in the fact that the size of the isopoly-cations formed can be strongly dependent on the nature of the anion, whereas in the formation of the isopoly-acids the cation exerts no recognizable influence. Finally, the attainment of hydrolysis equilibrium succeeds in general appreciably more slowly with the isopoly-bases than with the isopoly-acids, although slowly moving processes can also occur with the latter, like the aggregation processes with freshly prepared silicic acid solutions.

Fundamentally, the latter fact, which because of its very nature often renders the making of observations which can be interpreted in detail considerably more difficult, must from the first be placed in the foreground. In the hydrolysis of salts of weak acids, as appears from the results, one is not dealing with final equilibria in solution, as is usually the case with isopoly-acids, but with metastable equilibria. Yet these, provided the establishment of the next step does not take place too quickly, can be considered on their own and analyzed. One must then, however, be quite clear about the fact that the establishment of a reversible equilibrium, which can be defined, is frequently followed by an irreversible aging. The products arising from the latter are to be kept separate from the ions taking part in the equilibrium. It must further be considered that the position of the rapidly established hydrolysis equilibrium, as also the rate of aging, is greatly dependent on the hydrogen-ion concentration. But since the kind of aging is, for its part, dependent on the position of the preceding hydrolysis equilibrium, the rate at which the final stable state is reached — with the precipitation of hydroxide on exceeding its solubility product — can, under certain circumstances, depend in a really singular way on the hydrogen-ion concentration²³¹. Thus a 0.1-*N* aqueous solution of ferric perchlorate already precipitates hydrated ferric oxide after 2 days, whereas one treated with 0.5 moles of caustic soda shows a slight precipitate only after a matter of weeks: with 0.2 moles of alkali the solution is still clear after 2 months, but with 2.5 moles, on the contrary, the iron is again precipitated quantitatively as the hydrated oxide after a few days. The aging of the hydrolysis product preponderating in the pure aqueous solution is greatly accelerated by hydrogen ions. If the concentration of the latter is diminished by the addition of alkali, the aging is slowed up. The hydrolysis equilibrium is simultaneously displaced, and if much alkali is now added, an isopoly-base finally participates in it that

²²⁹ G. JANDER and A. WINKEL, *Z. anorg. Chem.*, 1930, **193**, 1; G. JANDER and K. F. JAHR, *Kolloid-Beihefte*, 1936, **43**, 323.

²³⁰ See p. 232, footnote 233.

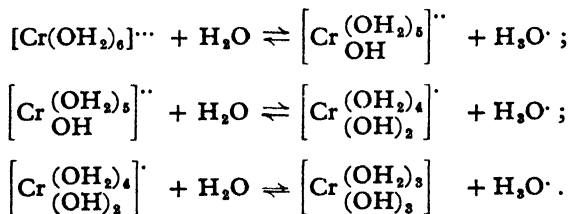
²³¹ G. JANDER and K. F. JAHR, *Kolloid-Beihefte*, 1936, **43**, 330.

is no longer capable of existence for any length of time in the alkaline region, so that, as a consequence, the point of precipitation is now reached. Because numerous isopoly-bases may be present in solution, each possessing its own solubility and its own rate of aging, or, more generally, its own peculiar properties, the situation becomes extraordinarily involved.

It is here possible to predict on the strength of the co-ordination theory just how large the variety can be. The isopoly-bases of trivalent chromium may be chosen as an example, since these have been especially thoroughly investigated by a number of investigators from various angles^{232, 233, 234}. (In this, the special suitability of chromic salts for the tanning of leather has played its part, these being preferable to those of aluminium and trivalent iron.) A logical application of the co-ordination theory to these was originally undertaken by BJERRUM²³² and still more particularly by STIASNY²³³.

In order not to make the considerations too complicated from the start, the above-mentioned factors which are operative in the formation of isopoly-cations will be dealt with individually. The influence of the anions on the process will therefore remain unconsidered at first. The question of aging will also be set aside. Solely the changes which the aquo-cations can undergo will be examined now.

The hydrolysis of the hexaquo-chromic ion is completed in stages according to the following scheme (cf. Chapter XI, 3, (iii)):



The non-electrolyte $(\text{H}_2\text{O})_3\text{Cr}(\text{OH})_3$ will probably not be stable in solution, but be precipitated as hydrated chromium sesquioxide²³⁵.

In a solution of a chromic salt, only the first stage of the hydrolysis will take place to a predominating extent. The second and third will become noticeable only on the addition of increasing quantities of alkali. It is to be expected that, if an appreciable amount of the last stage is arrived at by the adequate removal of H^+ , hydrated oxide will be precipitated.

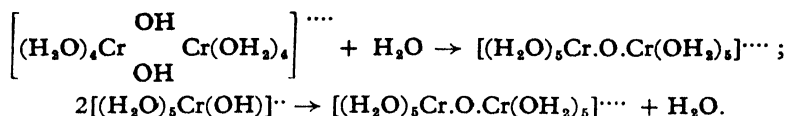
The hydroxo-aquo-ions from the first two stages can now combine to

²³² N. BJERRUM, *Z. physik. Chem.*, 1907, **59**, 581; 1910, **73**, 724; 1924, **110**, 656; N. BJERRUM and C. FAURHOLT, *ibid.*, 1927, **130**, 584.

²³³ Tanning with chromium: E. STIASNY, *Gerbereichemie*, pp. 347 ff and 534 (Dresden, 1931).

²³⁴ G. DENHAM, *Z. anorg. Chem.*, 1908, **57**, 380; J. SAND and F. GRAMMLING, *Z. physik. Chem.*, 1908, **62**, 1; A. KÜNTZEL and G. KÖNIGFELD, *Collegium*, 1935, No. 782 VI, 257; A. KÜNTZEL, C. RIESS and G. KÖNIGFELD, *ibid.*, p. 270; C. RIESS and K. BARTH, *ibid.*, 1935, No. 778 II, 62; G. JANDER and W. SCHEELE, *Z. anorg. Chem.*, 1932, **206**, 241.

²³⁵ In other cases, non-electrolyte aquo-complexes of this type are stable, namely if a halogen takes the place of the OH, as in $(\text{H}_2\text{O})_2\text{CuCl}_2$, for example (cf. p. 137).



The former process is more probably that which occurs.

To distinguish it from ol-bridge-formation, this kind of condensation may be named dehydration.

Again the most varied water-poorer complexes can be formed according to this scheme. But as the final stage of these irreversible condensation processes, a hydrated oxide HCrO_2 , corresponding stoichiometrically to goethite HFeO_2 , might be attained after a very long time²³⁷.

The processes of ol-bridge-formation and of aging, which within a certain p_{H} region take place with the chromic salts at rates so different that they can, for all essential purposes, be kept apart in time, need not possess this distinguishing characteristic in all cases. Thus, in the case of the aluminium salts, they appear to overlap in time to a considerable extent. A method which, like the diffusion method, provides only the approximate molecular weight of the cationic complex is naturally not able to differentiate between the two theoretically predictable possibilities of aggregation of the complexes arising through hydrolysis²³⁸.

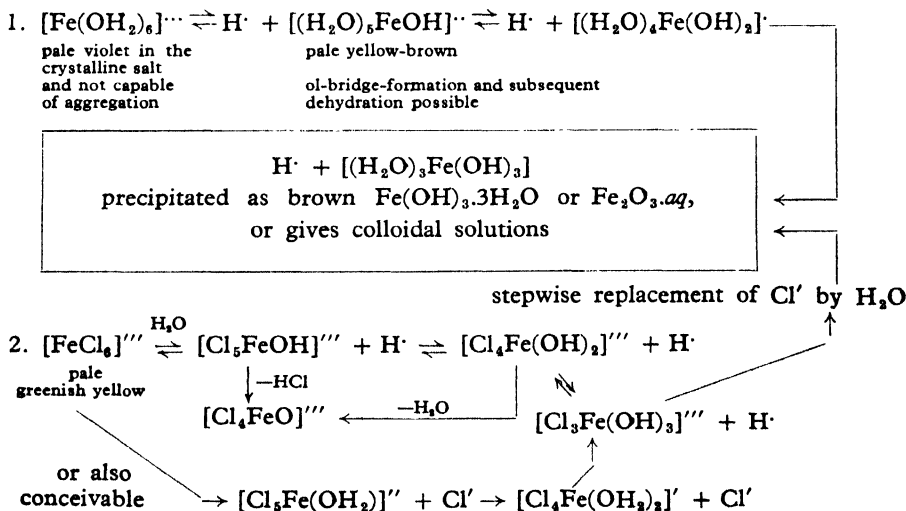
The variety of possible complexes from the two primary monomeric aquo-hydroxo-ions $[(\text{H}_2\text{O})_5\text{CrOH}] \cdots$ and $[(\text{H}_2\text{O})_4\text{Cr}(\text{OH})_2] \cdots$ arising through hydrolysis is already very large as it stands. It is now increased still further by the fact that under certain circumstances the anion is able to take part in complex-formation. Herein is found an explanation of the initially surprising influence it exerts on the kind and velocity of formation of the more complex isopoly-cations. At the same time, however, it also becomes understandable why, with the isopoly-anions, an influence due to the cations is not found. In the formation of typical acid-complexes, metal atoms are not able to take part, so that this complication is absent. The manner in which the anion intrudes can differ according to its nature and the experimental conditions. Either it displaces solely aquo molecules or hydroxo groups, or it takes the

²³⁷ W. IPATIEW and A. I. KISSELEW, *Ber.*, 1926, **59**, 1418; W. IPATIEW and B. MUROMZEW, *ibid.*, 1927, **60**, 1980; A. SIMON, O. FISCHER and T. SCHMIDT, *Z. anorg. Chem.*, 1929, **185**, 112. Concerning the way in which this transition is to be thought of in the hydrolysis of bismuth salts, and how here relationships exist with the lattice structure of the bismuth oxyhalides (Chapter VIII, 7, (v)), see F. GRANÉR and L. G. SILLÉN, *Acta Chem. Scand.*, 1947, **1**, 631 (measurements of equilibria in the hydrolysis of Bi salts).

²³⁸ The presentation given here differs from that given by G. JANDER and K. F. JAHR (*Kolloid-Beihfte*, 1936, **43**, 337 ff), inasmuch as it at the outset places the ol-bridge-formation in the foreground, and especially in that it proceeds from the hexaquo-chromic ion, as does BJERRUM's presentation, and not from an undissociated salt as according to JANDER and JAHR. The latter, in dealing with the basic salts considered as arising through hydrolysis, consequently trail the anion everywhere with them, as in, e.g., $\text{Cr}(\text{H}_2\text{O})_6(\text{NO}_3)_2\text{OH}$, and join it to the central atom partly (as with basic ferric perchlorate) with the same valence-line as is used for the oxygen atoms which link metal atoms, thus resulting in calculated molecular weights that differ appreciably from those which would be derived for the aggregated ions.

place of ol groups in the bridge links and appears as the connecting principle. In acid solution, the displacement of aquo molecules can, under certain circumstances, proceed to such an extent that the metal atom becomes the centre of an anionic complex. Thus, in acid solutions of ferric chloride, for example, the complex FeCl_6''' analogous to the much stabler FeF_6''' can arise, which with water may become hydrolyzed in stages to $[\text{FeCl}_5(\text{OH}_2)]''$, etc.²³⁹ If it is desired to eliminate complications of this kind, then, with JANDER and his collaborators, the perchlorates must be chosen as salts, since so far no case is known of the perchlorate ion appearing as a perchlorate-complex bound in the first sphere or as a bridge member in polynuclear compounds. The perchlorate ion thus means no competition for the aquo, hydroxo or ol groups.

Apart from all the complications which arise through the possibility of formation of additional anionic complexes of the metal when certain anions are chosen for the salts of weak bases, the formation of the hydrated oxide in the case of a weakly basic, amphoteric hydroxide would further appear, without considering the aggregation and aging phenomena, to be formally attainable from two sides. This will be briefly illustrated by formulae for the instance of the last-mentioned example with iron as the central atom (H_3O^+ being written H^+ for simplicity):



Which processes occur depends on the acidity of the solution and the nature of the anionic component, as well as first and foremost on the central atom. In the hydrolysis of the not decidedly saltlike halides of metals that are not typical cation-producers, the hydrolytic processes in the formation of hydrated oxides corresponding to the second mechanism will play the chief if not the exclusive rôle. Basically, the possibility of formation of

²³⁹ Cf. in this respect R. SCHWARZ and G. MEYER, *Z. anorg. Chem.*, 1927, **166**, 190.

polynuclear anionic complexes through ol -bridge-formation, or in this case more probably through dehydration, also exists here. The observations carried out on the hydrolysis of the zirconyl salts belong here²⁴⁰.

Once again, it is seen here very clearly how the co-ordination theory is able to provide valuable formal guides for the structural possibilities and courses of reaction. In general, however, it does not result in detailed decisions between the predictable structures, but rather in obtaining — only approximately and much less definitely than with the isopoly-acids — limiting conceptions of the ions occurring in solution and their molecular magnitudes.

²⁴⁰ G. JANDER and K. F. JAHR, *Kolloid-Beihfte*, 1936, **43**, 315 (also literature relating to the anionic zirconyl complexes such as $[ZrO(SO_4)_2]''$ and $[ZrOCl_4]''$).

BOOK II

ATOMIC STRUCTURE AND CHEMICAL BONDING

CHAPTER IV

THE PERIODIC SYSTEM OF THE ELEMENTS AND THE STRUCTURE OF THE ATOMS

1. Comparative Examination with the Aid of the Periodic System

The Periodic System erected by MENDELÉEF and LOTHAR MEYER provides a systematic ordering of the *elements* which is ingeniously correlated with their physical as well as their chemical properties. Its significance extends still further, however. Precisely on account of this ordering it permits, as long as elements remain which are still unknown, the chemical and physical properties of these elements and even of their compounds to be predicted. With gifted insight, MENDELÉEF, as is well-known, perceived the gaps which still existed in the System in his time and filled them with elements whose properties he foretold¹. He based his predictions upon skilful interpolations between the properties of the period-neighbours as well as of the group-neighbours. This anticipatory manner of thinking was also often employed subsequently in predicting the physical and chemical properties of unknown compounds of known elements. This was relatively easy when analogous compounds of the neighbours in the system were available. If, conversely, within a given series of measurements the numerical values found within a group or period did not exhibit the expected trend, then one could state with a high degree of probability that one of the anomalous measurements must be wrong, and verification was often enough encouraged thereby. To name only one example, the boiling point of carbon tetrafluoride, for a long time given as -15° , could be seen to be incorrect, since in the fourth main period the boiling points, not only of the fluorides but of the halides quite generally, show a regular increase. Consequently CF_4 , which precedes silicon tetrafluoride SiF_4 with the sublimation point -90° , must boil still lower. Surprisingly enough, in this particular case no objective verification ever took place, but, during investigations aimed at other objectives, it has turned out that the sublimation point of CF_4 lies at -128° ².

For all that, one had here and there to accept irregularities in the trend of chemical and physical properties within a group for granted, as must still be done today. Thus, to quote an especially familiar example, with respect to the stability of its oxides and oxy-acids bromine is not intermediate

¹ D. I. MENDELÉEF, *Liebigs Ann. Chem.*, 1872, **Suppl.** 8, 196 ff.

² P. LEBEAU and A. DAMIENS, *Compt. rend.*, 1926, **182**, 1340.

between chlorine and iodine, as it is in its other compounds, but forms fewer and less stable compounds with oxygen than these elements. Indeed, one was even compelled to recognize as genuine an irregularity which depended upon the fundamental ordering principle of the System, namely arrangement according to atomic weights, and which, even after the most careful re-examination, could not be set aside. Iodine, which without doubt belonged to group VII, possessed with 126.92 a *smaller* atomic weight than tellurium belonging to group VI with 127.61. Also the less obviously "incorrect" order of atomic weights with cobalt and nickel, as also later with argon and potassium, proved to be real. Only advances in knowledge concerning the structure of atoms, the discovery of isotopic elements and their verification brought the explanation which originated in the fact that, even in the atomic weight, the ultimate ordering principle had not been found, but that this is provided by the atomic number. Here, as also in other less deeply marked irregularities which on occasions were to be found in the trends of the properties of similar compounds within a group or in progressing along a period, valuable indications of special and hitherto undiscovered connections were obtained. Examples of such peculiarities within a group are the relatively high boiling points of the hydrides of nitrogen, oxygen and fluorine in the first period relative to the hydrides of the elements of the later periods in groups V—VII (Chapter VII, 2, (ii)), and the anomalous boiling point of aluminium trimethyl (p. 169; Chapter VII, 9). An example of a progression within a period is the striking stability of the divalent ion of manganese in the transition metals with respect to the neighbouring Cr^{2+} and Fe^{2+} ions. Explanations have already been found for the examples quoted. Others still await clarification. At all events, as such examples indicate, the kind of thinking which involves the interpolation of properties, and which must perforce lead to a systematic treatment of the Periodic System with respect to the properties of certain classes of compounds, has reaped a rich harvest. It is especially strongly and characteristically marked with W. BILTZ and his school in the broadly planned series of investigations, *Beiträge zur systematischen Verwandtschaftslehre* (cf. p. 319, footnote 27). But is it also found successfully employed by various other investigators. In order more clearly to explain this way of thinking as it is practised now that the knowledge of atomic and molecular structure is so far advanced, the atomic-volume curve, outlined in the first place by LOTHAR MEYER, will be considered. As abscissa, however, is plotted not the atomic weight but the atomic number, and as ordinate the volume in cm^3 occupied by one g-atom at absolute zero (Fig. 29).

Since the majority of elements are metals and hence, in the type of bonding between the atoms, to a great extent comparable, the space occupied for metallic bonding of the atoms is reflected in a large portion of the atomic-volume curve. Its characteristic trend is determined not solely by variations in the spatial content for metallic bonding, however, but also appreciably

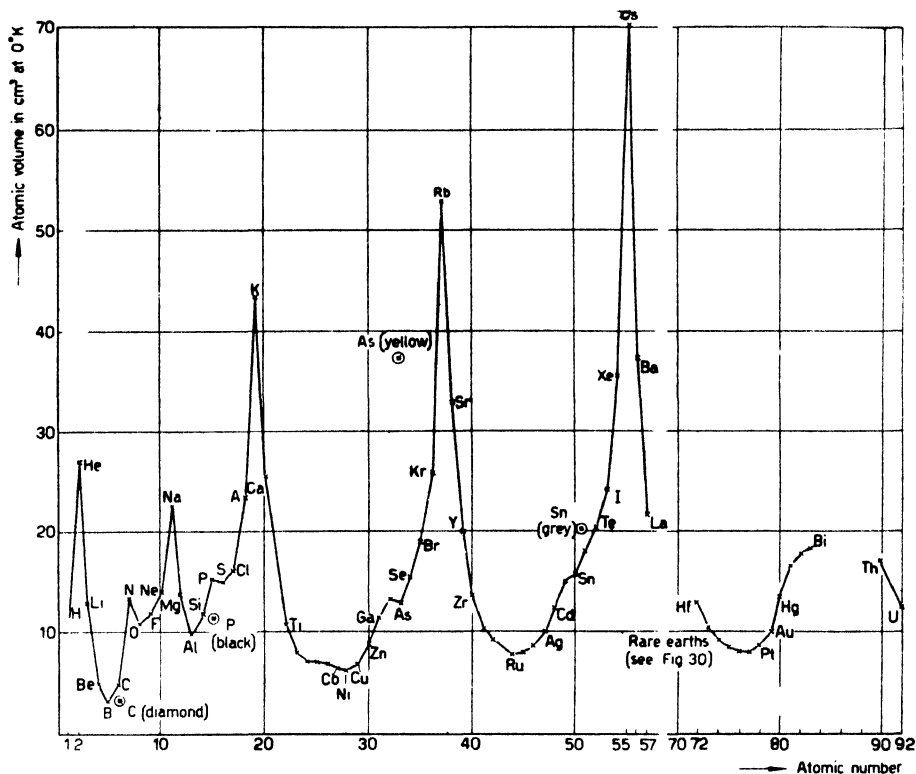


Fig. 29. Atomic-volume curve of the elements.

by the regular recurrence of non-metals in groups V, VI and VII. On account of the characteristic difference between metallic bonding and that which predominates between non-metallic atoms, it is of little consequence that the latter can vary considerably. Setting aside this variation in the state of bonding among the non-metals, one finds oneself with the latter in the main groups on the ascending branch of the curve, for the atomic packing in the liquid or crystalline non-metals, which like Cl_2 , O_2 , N_2 , S_8 and P_4 form molecular lattices almost exclusively, is not so close as in the metals. To be sure, within the molecules of the non-metals the atoms are situated really closely, appreciably closer than in the lattices of the metals. Thus the Br—Br distance in Br_2 is 2.28 Å, that of Fe—Fe in the lattice of α iron 3.68 Å. But on account of the weak intermolecular forces predominating between them, the non-metallic molecules are loosely packed. With the non-metals there are thus two factors which co-operate in determining the spatial content and which are not separated in the calculation of the atomic volume, namely the spatial content of the atom within the molecule and the spatial content of the molecule itself. Since the space required by the molecules increases as the intermolecular forces decrease, the atomic volumes increase from group V to group 0, the rare gases. For

the latter, which do not form molecules, the interatomic forces are by far the smallest, much smaller than the intermolecular forces for the halogens which precede them in the Periodic System.

Among the non-metals the trend of the atomic-volume curve is not always unequivocally fixed, inasmuch as polymorphism often occurs. In general, however, the different densities of the polymorphic modifications make little difference in the resulting spatial content of the atoms. Only in the cases of phosphorus and arsenic, according to which modification is selected, does the position of the atomic volume relative to that of the following element turn out differently. Thus white phosphorus with a density of 1.98 has almost the same atomic volume as α sulphur with density 2.07, whereas violet phosphorus of density 2.7 possesses an atomic volume which is decidedly smaller. The cause of the sometimes not inconsiderable differences in the spatial content of the atoms in polymorphic modifications of non-metals is to be sought in the different states of bonding in which they are to be found (Chapter VII, 10).

In the usually finer differences in the atomic volumes of polymorphic metals, a much less important rôle is played by polymorphism than with the non-metals, since, in consequence of the similarity in the metallic bonding, the variations in density of the polymorphic modifications are much slighter, and maintain themselves within the same limits as for polymorphic modifications of non-metals with similar bonding, like α and β sulphur. Sometimes the atomic volume remains practically the same, even when one modification possesses the cubic closest and the other hexagonal closest packing, as with calcium or cobalt. But also when, on the conversion of one modification into the other, the closeness of the packing changes, as, for example, when the cubic face-centred lattice representing a closest form of packing is converted into a body-centred packing, which is not closest packed, the variations in density are sometimes surprisingly small, as with the transition of α into γ iron (Chapter VIII, 9, (iii)). The change in volume actually to be expected, according to the models which can be constructed out of equivalent spheres, is here almost compensated by a change in the lattice forces. On comparing the atomic volumes of metals, it is seen to be generally a matter of indifference from which modification the atomic volume is derived for insertion into the curve. Tin constitutes an exception. Only as white tin does it fit into the curve, the grey modification, by way of contrast, possessing an atomic volume which is much too large.

The transition from non-metals to metals is reflected by four sharp peaks in the atomic-volume curve at the points where the alkali metals are situated, which peaks increase in height with increasing atomic weight. From these the atomic volume falls to the alkaline-earth metals, and then further to the ensuing metals. Of the alkali metals, only lithium is not situated at a peak owing to the unusually large atomic volume of helium which, with 27 cm^3 , exceeds both hydrogen with 11 and lithium with 12.6 cm^3 (referred

to absolute zero). The steep ascent in atomic volume from the rare gases to the alkali metals is not, as one might imagine, a natural continuation of the increase from the halogens to the rare gases, for the latter increase is to be ascribed to a diminution in the VAN DER WAALS forces of cohesion in passing from the halogens to the rare gases. In the case of the metals these intermolecular or interatomic forces no longer govern the spatial picture, as in these the valence electrons as interstitial electrons effect the very different metallic type of bonding between the atoms. Consequently the interatomic forces show a quite unusual increase in passing from the rare gases to the alkali metals. That the latter however possess much larger atomic volumes, is to be ascribed to the addition of new shells to those of the closed rare-gas shells. On this account, the "true" volumes of the atoms, when by this one means the spaces occupied by spheres whose radii are given by the distances between the atomic nuclei and the outermost electrons in the ground states, are much larger. In the trend of atomic volumes, this increase does not receive full expression in the sharp ascent from the rare gases to the alkali metals, since it is opposed by the increase in interatomic forces³. It appears in its total magnitude on comparing the effective cross-sections of the rare gases and alkali metals, as given by the diffraction of electrons for atoms of the gaseous elements.

Also in the drop in atomic volume from the alkali to the alkaline-earth metals and further to the metals of group III, the decrease in the true dimensions of the atoms does not receive expression. Such a decrease is certainly to be expected, since with increasing nuclear charge the attractive power of the nucleus for the electrons increases and effects a concentration of the surrounding electron cloud. But this decrease in the true atomic volume is not the factor which controls the trend in the atomic-volume curve. The interatomic forces of metallic bonding have a much greater effect. There are namely no unchanged atoms in the crystal lattice of a metal. Their valence electrons effect as interstitial electrons the cohesion between the cores of the atoms situated as charged ions in the lattice positions (Chapter X, 3, (i)). Their radii do indeed decrease with increasing nuclear charge for the same reason as for the free atoms, but the effect upon the measured atomic volume is only slight compared with that of the magnitude of the charge on the atomic core upon the interatomic forces, and hence upon the space occupied per atom. As one proceeds group to group within a period, the ionic charge of the atomic core increases as long as all the valence electrons take part as interstitial electrons in metallic bonding. It is this growth of charge with its resultant strengthening of the attraction which determines the decline in the atomic volume, as is shown, for example, on passing from the alkalis to the alkaline earths or from copper to gallium: the higher the ionic charge, the closer the packing in the lattice.

³ In the forementioned case of helium and lithium, it even brings about a drop in atomic volume on account of the unusually small interatomic forces with helium.

A proof that the magnitude of the charge on the atomic core in the metal lattice does indeed determine the atomic volume first and foremost, and not the volume of the ion considered as isolated (or that of the free atom), is to be inferred from the trend in the atomic-volume curve among the rare earths. Generally speaking, these vary only slightly in atomic volume, but two of them, *europium* and *ytterbium*, stand out with atomic volumes which are abnormally large (Fig. 30).

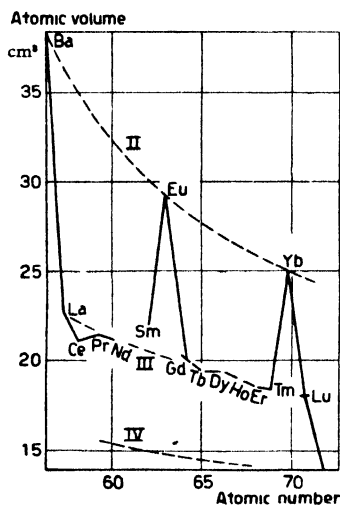


Fig. 30. Atomic-volume curve for the rare earths.

The cause of these two irregularities has been demonstrated with certainty by magnetic measurements (Chapter V, p. 392). In the lattices of europium and ytterbium divalent ions are present, while in those of all the other rare earths trivalent ions occur. Thus only two valence electrons are operative as interstitial electrons in producing metallic bonding in the lattices of europium and ytterbium, whereas there are three such electrons in the cases of the remaining rare earths. The influence of ionic charge on the atomic volume here masks all other influences, including that of crystal structure. It is not apparent from the atomic-volume curve that europium crystallizes in a body-centred cubic lattice, that is, not in one of closest packing, whereas most of the rare earths crystallize in hexagonal closest packing, and ytterbium in cubic closest packing.

The rare earths, viewed as a whole, again provide an example of the dependence of atomic or ionic size upon the influence of nuclear charge on the electron envelope. In the series commencing with lanthanum, the ionic volume diminishes regularly in consequence of the increasing nuclear charge. The outermost shell remains the same while one electron after another is fed into the inner N shell, until with lutecium it is completed and contains 32 electrons. This decrease in the volume with increasing mass of the nucleus is named the *lanthanide contraction*. It results in the

atoms and ions of the elements of the fifth period from hafnium onwards possessing about the same dimensions as those of the fourth. Upon this rests the extraordinary similarity of zirconium and hafnium and of niobium and tantalum in their compounds. Since, on passing from the fourth to the fifth period, the mass of the nucleus increases considerably, the lanthanide contraction is the cause of the high densities of the elements of high atomic weight. The following brief survey provides information concerning the increase in densities which occurs between the fourth and fifth periods while the atomic volumes remain almost the same ⁴:

	Zr	Hf	Nb	Ta	Mo	W	Tc	Re
atomic volume	13.97	13.42	10.86	10.88	9.4	9.5	—	8.86
density	6.52	13.31	8.6	16.70	10.22	19.30	—	21.0
	Ru	Os	Rh	Ir	Pd	Pt		
atomic volume	8.14	8.40	8.29	8.53	8.87	9.08		
density	12.49	22.7	12.41	22.65	12.03	21.47		

Melting and boiling points of the elements ⁵, or these and other properties of certain classes of their compounds, *e.g.*, the chlorides and oxides, can be considered in the same way as the atomic volumes of the elements. For many purposes, it suffices to follow semi-quantitatively the trend of the changes in properties within a group or within a period in order to obtain useful rules or principles. One of the best-known rules of this kind, which is especially important for the chemist, is the increase in basic properties of the oxides with increasing atomic weight within a group, and the reduction of their basic properties on passing from one group to the next in the same period. As soon as it is desired to dig deeper and gain a theoretical understanding of such regularities, which for a long time could only be assessed as empirical, a closer examination of the structures of the atoms and the activity of their electrons cannot be avoided. In the foregoing discussion on the atomic-volume curve, use has already been made in various places of the achievements which are due to the research into atomic structure since the investigations of N. BOHR. Thus, as in this case, the chemist can frequently accept as facts the concepts of the physicist, which the latter has laboriously derived with the aid of the quantum theory from the optical and X-ray spectra as experimental material. Since the chemist in many cases does not need to trouble about their theoretical derivation, he simplifies the presentation considerably.

That it is possible to adopt this course was first demonstrated to the chemist by the physicist W. KOSSEL ⁶ in his well-known theory of chemical bonding. This theory proclaims as its leading concept the striving of the atoms to form closed electron shells, the octets of the rare gases and shells of eighteen electrons. Thereby, without first asking why just those shells

⁴ Values according to W. BILTZ, *Raumchemie der festen Stoffe*, pp. 17—21 (Voss, Leipzig, 1934).

⁵ Review: W. FISCHER, *J. prakt. Chem.*, 1941, [ii], 158, 200.

⁶ W. KOSSEL, *Ann. Physik*, 1916, [iv], 49, 229.

with 8 or 18 electrons are especially stable, the characteristic valencies of many elements and hence also the composition of their compounds become physically understandable. In contrast to the older valence ideas which, like those of ABEGG with the concept of valence and contravalence, such being complementary to 8 (p. 36), attempted to arrange the phenomena systematically according to the Periodic System, KOSSEL's theory possessed no physical foundation that was really tangible. Only later did it appear that it had frequently surmised the correct state of affairs.

The tendency to form closed shells leads to the formation of ions with definite positive and negative valencies, and the attraction of oppositely charged ions to the formation of heteropolar compounds. The existence of ions whose outer shells contain no closed group of electrons, like Cr^{3+} , Mn^{2+} , Fe^{2+} , Fe^{3+} and Sn^{2+} , had admittedly to remain unexplained by the theory. But the theory of chemical bonding, which universally explained the origin of heteropolar compounds by the electrostatic attraction of ions, allowed many deviations from the simple picture of KOSSEL to be made manifest, without anything in the latter needing to be fundamentally changed. The only requirement was that, in place of a rigid closed shell, a sheath of electrons be assumed which could be modified under the influence of forces, in order to do justice to the phenomena by the introduction of ionic *deformation* or *polarization*⁷. For this, no conceptions of atomic structure are necessary, other than those which were employed by KOSSEL's theory in its original form.

The representation of the homopolar bond, which LEWIS and LANGMUIR drew up at almost the same time as KOSSEL shaped his theory of the heteropolar bond, also works with the concept of closed electron shells. In it, the significance of the shell of eight electrons receives expression in the *octet theory*, which has proved itself to be a useful guide in this electronic theory of valence. But the further development of this very theory, which for a time elevated the octet to a kind of dogma, teaches how the chemist cannot in the long run dispense with the physical foundation of his model; for, in order to rescue the octet theory in cases where it does not hold, otherwise well-founded concepts like the electron-pair bond have at times been abandoned, as in the explanation of the constitution of phosphorus pentachloride. In order not to have to assume that this compound contained a group of ten electrons, which, as we now know, is quite possible theoretically (pp. 270, 415), unpaired electrons or singlet links were arbitrarily assumed. Such errors were possible because the chemist did not concern himself with the causes which led to the completion of different electron shells. The relationships are by no means so simple that only completed shells of eight or eighteen electrons are invariably striven for.

⁷ In particular, K. FAJANS worked successfully with this concept: *e.g.*, *Naturwissenschaften*, 1923, 11, 165; *Z. Physik*, 1924, 23, 1 (with G. Joos); *Z. Krist.*, 1928, 66, 321. In addition, KOSSEL himself had already provided for deformation of ions in his theory.

If it is desired to draw finer distinctions in the manner in which the individual shells are filled, which is necessary for understanding the formation of many compounds as well as their properties, then the eight or eighteen electrons in a shell must be considered as divided into subgroups. The number of electrons to be included in the individual subgroups are known from data provided by the interpretation of spectra with the help of the quantum theory. The chemist can also accept these, to a certain extent unquestioningly, from the physicist. Still without precise knowledge of these subdivisions, KOSSEL was already able to point to the significance of incomplete shells in elements and ions and explain at least qualitatively their connection with certain physical properties, namely colour and paramagnetism. A deeper knowledge of the possibilities of filling these shells has today rendered even a quantitative treatment of paramagnetism possible. For this, however, the numbers of the electrons in the individual subgroups no longer suffice. Nor are these adequate when one wishes to grasp the refinements concerning the chemical bond or the physical behaviour of substances. Here a knowledge of the energy relationships for the different ways of filling the electron groups is also needed. In this, however, the chemist can no longer forgo a knowledge of the derivation of those "mystic" numbers with which he is provided by the physicist. Even the latter is still frequently unable to give the chemist the desired information, and for the time being the chemist must as hitherto be content to accept many experimental facts concerning the formation of compounds without question. A solitary example of this inability will be given.

The chromium atom with atomic number 24 possesses in its state of lowest energy, the ground state, the following electronic configuration (p. 271):

shell	K	L	M	N
total number of electrons	2	8	13	1
subgroups (see p. 271)	<i>s</i>	<i>s p</i>	<i>s p d</i>	<i>s</i>
number of electrons	2	2 6	2 6 5	1

The outermost N shell contains 1 electron. Accordingly it might appear at a casual glance as if monovalence would be a favoured valency with chromium. But, as is well-known, this is not the case. The reason for this is that electrons can still be removed easily from the uncompleted M shell with its uncompleted *d* subgroup whose energy level is only slightly different from that of the electron in the N shell. In the last resort, all 5 electrons can be removed from the *d* subgroup — the *p* subgroup, being complete and forming together with the *s* group a closed octet, is not touched—so that the hexavalency of chromium which follows from the Periodic System appears immediately comprehensible. But the additional, especially pronounced trivalence of chromium does not follow from the numerical

scheme, and even today the point has not yet been reached where its prominence is theoretically understood. Nor is the theory yet able to explain the occasional appearance of other stages in the oxidation of this element, as, for example, divalent chromium which, when aqueous solutions are not being worked with, is not so very unstable; or pentavalent ⁸ and possibly also tetravalent chromium in various organochromium compounds ⁹. With manganese, on the other hand, preference for the divalent state and the special properties of the compounds of divalent manganese can be understood, as, for example, their pale colour (pink) compared with those of the compounds of the other divalent transition elements (Chapter X, 6, (ii)). In general, however, if it is desired to progress to the point where many of the chemical peculiarities of the elements and their compounds still not understood today may be comprehended, then one must be familiar with the physical foundations of atomic and molecular structure. It has to be realized that this will not be accomplished by numerical considerations alone, in the manner which has somehow usually been practised since the concept of valency came into being. Even as a chemist, therefore, one should not be content merely to know what the physicist has produced concerning atomic structure, but must become acquainted, at least in main outlines, with the essential paths and thought processes which have led up to the present-day knowledge of the subject. Errors to which one can easily be led by a formal development of theoretical aids that are not completely understood will then be avoided.

2. The Periodic System and the Extra-nuclear Structure of the Atoms. The Line Spectra of Hydrogen and the Alkali Metals

(i) Models of the Atom and X-ray Spectra

It was possible to arrive at far-reaching conclusions with the help of the Periodic System, as illustrated here by examples, only after clarity regarding the structure of atoms, at least in broad outline, had been obtained. Modern conceptions, which, both experimentally and theoretically, are well-founded, go back to the model postulated by RUTHERFORD of a very small, positively charged atomic nucleus surrounded by a voluminous sheath of electrons. This picture, which LENARD had framed in a slightly different form as early as 1903, was obtained by RUTHERFORD from experiments on the deflection undergone by α -particles in the field surrounding the atom on their passage through matter. But its application to the Periodic System became possible only after optical and X-ray spectra had provided an insight into the structure of the surrounding envelope of electrons and it had become

⁸ W. KLEMM and A. NEUBER, *Z. anorg. Chem.*, 1936, **227**, 261 (magnetic measurements).

⁹ Compilations: F. HEIN, *J. prakt. Chem.*, 1931, [ii], **132**, 59; *Z. angew. Chem.*, 1938, **51**, 503.

recognized that the position of an element in the system was determined by the atomic number, which is equal to the positive charge on the nucleus and thus equal to the number of extra-nuclear electrons¹⁰. The atomic numbers of the elements follow from the X-ray spectra according to the well-known MOSELEY's law

$$\sqrt{\nu} = c(Z - a).$$

In addition, the series of lines occurring in the spectra, denoted as K, L, M and N series, enable the electrons to be subdivided into groups of electrons bound with varying degrees of tightness. These, once they have been formed, persist in all of the subsequent elements, this following according to MOSELEY's law from the regular changes in frequency of a particular X-ray line stipulated by the variation in nuclear charge. It is clear that these groups are collected into shells¹¹ which surround the nucleus of the atom at increasing distances, and are designated as K, L, M and N shells according to the X-ray series to which they correspond. In actual fact, the series belonging to any particular shell is not initially observed with the first element in which the shell is completed, but first with elements possessing a considerably higher atomic number. Thus, for example, the L series is first encountered with zinc with atomic number 30, whereas the L shell is already completely filled with neon with atomic number 10. The periodicity in properties of the elements according to the Periodic System then follows from the fact that each shell is able to contain only a limited number of electrons, and when it is completed the addition of a new shell begins. Chemical properties, in particular the valency of the elements, are then determined by the outermost shell of electrons. These comprise the determining factor for the optical spectra. It was the interpretation of these optical spectra which first made it possible to conceive the structure of the shells in detail and, in particular, to establish theoretically the number of electrons to be housed in the individual shells. This commenced with the work of N. BOHR, and, in the hands of SOMMERFELD, HEISENBERG, SCHRÖDINGER and others, finally led to a development of the quantum theory that was able to explain the Periodic System completely.

The hypothesis expressed by RUTHERFORD in his model of the atom, namely that an atom consists of a small positively charged nucleus and an envelope of electrons surrounding it, also led to the derivation of the finer structure of this envelope from the spectra. The first successful step taken in this direction was made by BOHR when, with his well-known model of the atom in which electrons revolve round the atomic nucleus in discrete orbits, he attempted to link the structure of spectra with the quantum theory. The further development of these ideas led eventually to a perception of

¹⁰ This was first expressed as a hypothesis by A. VAN DEN BROEK, *Physik. Z.*, 1913, 14, 32.

¹¹ W. KOSSEL, *Ann. Physik*, 1916, [iv], 49, 237; J. J. THOMSON, 1911; A. VAN DEN BROEK, *loc. cit.* (footnote 10).

the structure of the electron envelopes of all the elements, and hence also to an understanding of the periodic recurrence of properties as expressed by the Periodic System. In this, to be sure, BOHR's lucid model with the electron orbits had to be dropped to make room for a less straightforward description. In the latter, the state of each electron in the atom is exhaustively described by four numbers, the so-called *quantum numbers*. Two only of these sufficed to fix the orbit in the classical, imperfect model of BOHR. By virtue of their quantum numbers and the energies which these stipulate, the electrons can be collected together into shells and groups. Today the quantum theory is in a position to state precisely for any given atom how many electrons are contained in each shell and in each group, and the maximum number of electrons which can be contained in a particular shell or group. For his purposes, the chemist may be generally satisfied with these final pronouncements of the theory, and fall back upon the table in which these numbers are reproduced (pp. 271, 272). But where there is a dependence not only upon the application of rules which in themselves are not understood, but also upon their comprehension, he cannot ignore the manner in which these results have been derived. Even if he does not need to follow this in all its mathematical details, he should obtain a knowledge concerning which experiments have brought physics to an understanding of the Periodic System from the standpoint of atomic structure.

These experiments by which information concerning the electrons in the atom has been obtained have as object the determination of the interaction of matter with electromagnetic radiation and the influence of a magnetic field. They fall into two groups. The first group comprises the observation of spectra as they usually appear, the second the observation of spectra in a magnetic field, whereupon the spectral lines appear as split through the so-called *ZEEMAN effect*. Between the two groups, which in accordance with the historical development will be discussed separately, there is something fundamental to say concerning the magnetic theory. The description given here will follow essentially from the empirical standpoint and from the outset be orientated towards the object of bringing atomic structure into relationship with the Periodic System. Accordingly, the considerations begin with the spectrum of the simplest atom, the hydrogen atom.

A few general remarks concerning the possible spectra for an element will be made beforehand. The spectrum of an element depends upon the conditions under which it is induced to emit spectral lines. As a generalization it has been customary to distinguish these conditions by use of the terms arc spectra and spark spectra. The *arc spectrum* corresponds to light emission from an atom, the *spark spectrum* to light emission from an atom ionized one or more times. The two spectra are completely different for the same element, since, as will be demonstrated subsequently, the line series in a spectrum, as also the finer structure of the spectral lines, depends upon the number of the electrons which are able to co-operate in the emission

It often happens that unionized and ionized atoms are caused to emit simultaneously under the conditions of excitation. In this event, arc and spark lines appear side by side. Which lines belong to the uncharged atom and which to the various positively charged ions can be determined by the action of electric and magnetic fields on canal rays. In the latter only the ionic emitters occur, from the deflection of which the magnitude of their charge can be calculated provided their masses are known. The lines of the alkali and alkaline-earth metals observed in the Bunsen flame originate only in the emission of atoms. In the case of barium, the green lines belong in part to the barium atom and in part to singly ionized barium. For hydrogen only an arc spectrum is possible, since the ionized hydrogen atom no longer possesses an electron. But, in addition to the H atom, the H_2 molecule is also able to give a spectrum which is completely different from that of the atom. In the usual excitation of hydrogen to emission, as for example in the GEISSLER tube, the molecular spectrum does not appear. Throughout the following only the arc spectra derived from the uncharged atoms of the various elements will be considered.

(ii) The Line Spectrum of Hydrogen

The lines of the familiar hydrogen spectrum can be arranged into a series in which, as discovered by BALMER, the frequencies obey the simple law:

$$\nu = \frac{c}{\lambda} = c \cdot R \left(\frac{1}{2^2} - \frac{1}{n^2} \right).$$

For the red hydrogen line n is to be put equal to 3, for the blue equal to 4, and so on, n representing all the whole numbers. Towards the end of the series the lines converge closer and closer together to the limiting value $\frac{1}{4}c \cdot R$ for $n = \infty$.

In addition to this BALMER series, there are other series in the hydrogen spectrum, for whose lines very similar formulae apply. The general expression, which includes that for the BALMER series, takes the form:

$$\nu = c \cdot R \left(\frac{1}{n_2^2} - \frac{1}{n_1^2} \right).$$

For each value of n_2 , a new series is obtained when n_1 is allowed to run through the sequence of whole numbers. Accordingly, n_1 and n_2 , which may assume all the integral values, are named *running numbers*, n_1 naturally being always larger than n_2 . All the lines of the hydrogen spectrum are reproduced by this *generalized BALMER formula*.

If, instead of the frequency $\nu = \frac{c}{\lambda}$, one works with the wave number $\tilde{\nu} = \frac{1}{\lambda}$, then the wave number of a spectral line of hydrogen appears as the difference between two spectral terms $\frac{R}{n^2}$, where $n = 1, 2, 3, \dots$

The constant R , the *RYDBERG constant*¹², is a universal constant, for it is valid not only for all the various hydrogen series, but also for all other line spectra, for example those of the alkali metals. Its numerical value is $109,677.581 \text{ cm}^{-1}$.

The generalized *BALMER* formula holds with extraordinary precision. Yet it is not complete, for it does not take account of the fact that the lines of the hydrogen spectrum are not simple lines, but possess a *fine structure*. They are mostly doublets. Allowance for this fact can be made by a minor modification in the formula, with which we do not need to concern ourselves here.

The *BALMER* series finds its theoretical explanation by means of the quantum theory. According to the latter the emission of light takes place in a quantized manner by the release of energy quanta whose dimensions are determined by *PLANCK's* elementary quantum $h = 6.624 \times 10^{-27} \text{ erg sec}$. In order to be able to effect such an emission, the hydrogen atom must be brought beforehand from its state of lowest energy, the *ground state*, to an energy-richer *excited state* by the absorption of energy. This excitation of the hydrogen atom consists of removing the electron further away from the nucleus. The different stages of excitation result by the quantized assumption of energy. Based on a picture of the structure of the atom drawn up by *BOHR*, one used to say that on excitation the electron was raised to a "higher" orbit, and that on the emission of light it went over from a "higher" to a "lower" orbit. According to the original atomic model of *BOHR*, which can no longer be maintained in this simple pictorial form, the electron revolves round the hydrogen nucleus in various discrete tracks, whose radii are determined by elementary quanta, the charge and mass of the electron, the charge of the hydrogen nucleus and the *quantum numbers*, that is to say, the sequence of whole numbers beginning with 1¹³. Without going into the details of *BOHR's* model of the atom, for which the energies of the individual tracks are calculated in the classical manner, it will suffice here in the first place to retain *BOHR's* assumption, which is independent of the special peculiarities of the model. In accordance therewith, there is a connection between the frequency $\nu_{1,2}$ of the light emitted and the difference in energy of the atomic states, the emission of light being the result of a transition from one state into the other. According to *BOHR*, the relationship

¹² The velocity of light is frequently included in the constant, which thereby gains the dimension of a frequency, namely sec^{-1} . The *RYDBERG* frequency cR , thus defined, has the dimension $3.29 \times 10^{15} \text{ sec}^{-1}$.

¹³ The angular momentum $mr^2\omega_n$ of the electron considered to be revolving round the nucleus becomes quantized as integral multiples of $\frac{h}{2\pi}$, that is, assumes the values $\frac{n \cdot h}{2\pi}$ ($n = 1, 2, 3, \dots$). The proof that it is the angular momentum which is to be quantized cannot be reproduced here. In addition, the rotation of the electron about the nucleus is calculated with the assumption of a classical field of force. A positive nucleus with the charge number $Z, = 1$ in the case of hydrogen, exercises *COULOMB* attraction on the electron of charge e and mass m .

$$h\nu_{12} = E_{n_1} - E_{n_2} \quad (n_1 > n_2) \quad (\text{BOHR'S frequency condition})$$

holds when a transition occurs from energy level E_{n_1} (the n_1 th orbit) to energy level E_{n_2} (the n_2 th orbit). In each E value is to be found, in addition to the forementioned universal constants h , e and m and the characteristic nuclear charge of 1 for the hydrogen atom, only the *quantum number* n , and that in a way which corresponds exactly to the generalized BALMER formula when the above equation is converted to the equation for the wave number $\tilde{\nu}$ by dividing by hc . In this way, an expression for the RYDBERG constant is simultaneously obtained, this being composed only of universal constants:

$$\tilde{\nu}_{n_1, n_2} = \frac{2\pi^2 me^4}{h^3 c} \cdot \left(\frac{1}{n_2^2} - \frac{1}{n_1^2} \right); \quad R = \frac{2\pi^2 me^4}{h^3 c} = 1.09 \times 10^6 \text{ cm}^{-1}.$$

Agreement with the foregoing experimental value is satisfactory.

The *quantum numbers* which occur in the formula for the discrete energy levels of the electron are identical with the *running numbers* in the generalized BALMER formula. In more complicated spectra, to which we will now transfer our attention, a similar equation does not always prove applicable.

(iii) The Line Spectra of the Alkali Metals

The structure of the line spectra of the alkali metals is similar to that of the hydrogen spectrum, but they contain more spectral lines and series¹⁴. Accordingly, otherwise than for hydrogen, a *single* term does not suffice for the derivation of all the series. Here also it is fundamentally possible to reproduce the frequencies of all the lines by means of terms. Again, each line appears as the difference of two terms. To be sure, each term is not so simple as the BALMER term, for which the expression

$$\frac{R}{(m + \Delta)^2} = \frac{R}{\dot{n}^2}$$

is substituted. Once again m is the *running number*, an integer, and Δ is a correction which, as a first approximation, may be regarded as constant. It can assume positive and negative values. The number \dot{n} appearing in the place of the running number in the BALMER term is not a whole number, but the more nearly approaches such, the smaller the correction Δ . In anticipation, it may be stated that in this case the running number m may again be identified with the quantum number n , as for the hydrogen spectrum. If, however, the so-called *effective quantum number* \dot{n} deviates strongly from a whole number, then, since Δ may be positive or negative, it is not possible

¹⁴ The spectra of the singly ionized alkaline-earth metals, since they possess *only one* optically emitting electron, are constructed like those of the alkali metals. Spark spectra of the alkaline earths and arc spectra of the alkalis correspond to each other. On the other hand, the spectra of the alkaline-earth atoms with *two* optically emitting electrons have quite a different structure. Cf. p. 266 ff.

to say without further knowledge whether the running number m agrees with the true quantum number or not.

The various series in the spectra of the alkali metals correspond to different sequences of terms. The most important series in the alkali-metal spectra are the following, in which the nomenclature reflects in part the appearance of the lines:

- principal series, p ;
- second subordinate or sharp series, s ;
- first subordinate or diffuse series, d ;
- BERGMANN or fundamental series, f .

Further series are denoted alphabetically by g, h, \dots

For potassium¹⁵, for example, the term expressions for these most important series observed in the arc spectrum appear as follows:

$$p, \quad \tilde{\nu} = R \left[\frac{1}{(4 - 2.2299)^2} - \frac{1}{(m - 1.7652)^2} \right] \quad (m = 4, 5, 6, \dots);$$

$$d, \quad \tilde{\nu} = R \left[\frac{1}{(4 - 1.7652)^2} - \frac{1}{(m - 0.1465)^2} \right] \quad (m = 3, 4, 5, \dots);$$

$$s, \quad \tilde{\nu} = R \left[\frac{1}{(4 - 1.7652)^2} - \frac{1}{(m - 2.2299)^2} \right] \quad (m = 5, 6, 7, \dots);$$

$$f, \quad \tilde{\nu} = R \left[\frac{1}{(3 - 0.1465)^2} - \frac{1}{(m - 0.01)^2} \right] \quad (m = 4, 5, 6, \dots).$$

Since the lines are not all single, but are in part doublets, not all the terms can be simple. In point of fact, for one term, namely that with the correction $\Delta = -1.7652$, a second term lying very close with $\Delta = -1.7682$ is to be inserted. Strictly speaking, for the corrections -0.1465 and -0.01 two numbers should be inserted, which however lie much closer to one another. The term with $\Delta = -2.2299$, by way of contrast, is always single.

It is seen in this example that not all the conceivable combinations of terms occur. Similar terms do not in general combine among themselves. This is not only true for potassium, but also in other cases. For example, there are no spectral lines which can be represented by the expression

$$\tilde{\nu} = R \left[\frac{1}{(m_1 - 2.2299)^2} - \frac{1}{(m_2 - 2.2299)^2} \right] \quad (m_2 > m_1),$$

as would correspond to the difference between terms for the hydrogen spectrum. Rather, a term with a definite running number is held constant throughout, from which another term with a variable running number m must be subtracted. This term which varies with the running number is characteristic for the particular series, and is therefore identified with the latter for the same series. Thus, in the above example, the term with the correction -1.7652 is the p term, that with $\Delta = -0.1465$ the d term,

¹⁵ Of the potassium lines visible in the Bunsen flame, only the violet line at $404.5 \text{ m}\mu$ belongs to the principal series. The sodium D line is the only line of the principal series of sodium lying in the visible.

that with $\Delta = -2.2299$ the s term, and that with $\Delta = -0.01$ the f term. The s term, with running number 1 and so on, is abbreviated as $(1,s)$, $(2,s)$, $(3,s)$. The corresponding p sequence begins with the running number 2 and is written $(2,p)$, $(3,p)$. The d sequence begins with $(3,d)$ and the f sequence with $(4,f)$. Arranged according to the magnitude of the running number, the following possibilities of combination exist:

$$\begin{aligned} \text{principal series} & \dots \tilde{\nu} = (1,s) - (m,p) \quad (m = 2, 3, 4 \dots); \\ \text{2nd subordinate series} & \dots \tilde{\nu} = (2,p) - (m,s) \quad (m = 2, 3, 4 \dots); \\ \text{1st subordinate series} & \dots \tilde{\nu} = (2,p) - (m,d) \quad (m = 3, 4, 5 \dots); \\ \text{BERGMANN series} & \dots \tilde{\nu} = (3,d) - (m,f) \quad (m = 4, 5, 6 \dots). \end{aligned}$$

There exists, accordingly, yet another limitation than that which forbids the intercombination of similar terms, since:

- s terms combine only with p terms (principal series);
- p terms combine only with s or d terms (2nd and 1st subordinate series);
- d terms combine only with p or f terms (1st subordinate and BERGMANN series.)

If the terms are arranged in the sequence s , p , d , f , chosen according to ascending value of the lowest running number, $m = 1, 2, 3, 4$, naming s the first, p the second, d the third and f the fourth term series, it is then possible to formulate the following "selection rules" for the lines:

Only those lines occur whose term differences are given by two successive lines. In the former abbreviated symbolism, the term diagram, from which the respective terms for the combinations may be obtained, may be written:

$$\begin{array}{cccccc} (1,s) & (2,s) & (3,s) & (4,s) & (5,s) & \\ & (2,p) & (3,p) & (4,p) & \text{to} & \\ & & (3,d) & (4,d) & & \\ & & & (4,f) & & \\ & & & & (5,g) & \end{array}$$

A consideration of the structure of those lines which are doublets demands an extension of the scheme, so that all the terms with the exception of the s term must be doubly filled. Thus p should be replaced by p_1 and p_2 , d by d_1 and d_2 . The term splitting is the less extensive, the higher the numbers in the term sequence. In what follows, this structure of the lines can at first be disregarded. Later, however, important results are to be deduced therefrom (p. 257 ff).

The linking of observations made on the spectra of the alkali metals to the theory is not so straightforwardly possible as in the case of hydrogen, even when this simplification is allowed in the first place. Alone the fact that the running number m does not need to be identical with the natural principal quantum number creates difficulties. It is altogether impossible to base one's calculations on an atomic model consisting of a nucleus and a number of electrons in the manner possible for the case of hydrogen. Nevertheless, a conception linking on to the BOHR model of the hydrogen atom

proves to be serviceable. As for the latter, so with the alkali metals there is one electron, which may be briefly termed the *emission electron*, whose transition from a higher energy level to a lower one effects the emission of light. Here again the BOHR frequency condition

$$h\nu = E_1 - E_2$$

determines the frequency of the light emitted. Consequently there is a similarity between the structures of the alkali spectra and that of the hydrogen spectrum. Otherwise than for hydrogen, however, this electron is associated not with a nucleus but with an atomic *core*, in which the action of the nucleus Ze is "screened" by $Z - 1$ electrons. These, being very much closer to the nucleus than the emission electron, do not themselves come into play on the emission of light.

On account of the presence of these other electrons, the energy levels of this emission electron are no longer determined in each case by *one* quantum number, but by *several*. These tacitly appear in the dimension of the correction Δ in the BALMER term. In first approximation, expression can be given to the situation by means of a *second* quantum number, which takes its place by the side of the natural quantum number n .

Again making use of the picture of an electron moving in orbits round the nucleus, as in the model of the hydrogen atom, these orbits are not always circles whose radii are determined by the quantum number = running number n , but in the general case are ellipses, the eccentricity, the ratio of the major to the minor axis, being governed by the ratio of two quantum numbers, n and k . For the special case $n = k$, the orbit becomes circular. The second quantum number k is also named the *azimuthal quantum number*¹⁶. The magnitudes of the correction Δ are connected in such a way with this azimuthal quantum number that as k increases, that is to say the further one advances up the series s, p, d, f , the value of Δ becomes smaller in agreement with experience.

The new quantum theory departs from the pictorial representation of electron orbits. In place of the azimuthal quantum number, whose name goes back to the concept of orbits, use is made of the *subsidiary quantum number* l which is smaller by 1. Since in the explanation of the term expressions the question is one of justifying the insertion of whole numbers by the quantum theory, it is fundamentally immaterial, as long as no particular model is adhered to, from which number one begins to count the quantum jumps. If one puts $l = k - 1$, then for a circular orbit in the sense of BOHR's model

¹⁶ The size of the correction Δ can be approximately calculated if, as for the model of the hydrogen atom, the emission electron of charge $-e$ and mass m is regarded as subjected to the COULOMB attractive force of the screened nucleus of charge $Ze - 1$. The effect of this force is however less simple to apply than in the case of the hydrogen atom, since one is not dealing with a nuclear charge which may be regarded as concentrated at a point; but, on account of the composite nature of the atomic core consisting of a positive nucleus and negative electrons, in addition to the COULOMB potential, higher terms which arise through dipole and quadrupole action must also be considered.

$l = 0$: l has no longer the same meaning as k for the shape of the orbit of the old model. In the BOHR model, k measured the angular momentum of orbital motion. We now know that for the orbital motion of the electron, which may no longer be represented in the sense of BOHR's model, a measure of the orbital momentum is provided not by k , but by l , which is therefore also known as the *orbital-momentum quantum number*.

Among other things, a consideration of the fine structure of the lines in the spectra of the alkali metals leads to the recognition that the electrons do not move in BOHR orbits. It is also seen that the doublet structure of the lines can only be explained by the introduction of a further quantum stipulation. This is obtained by ascribing to the electron an angular momentum of its own, such being known as the *spin*.

(iv) Doublet Structure of the Spectral Lines of the Alkali Metals

It is generally known that the D line of sodium is a double line, a doublet with the wave-lengths 5890 and 5896 Å. Similarly other spectral lines of the alkali metals are not single, but doublets. Even in the case of hydrogen, though only with especially subtle aids, a doublet structure can be detected for the spectral lines, which here consist of double lines lying extraordinarily close to each other. There must therefore be two different energy values lying close together to which the emission electron can be raised before light emission. BOHR's original theory provides for only one, however, and consequently only a single line, as follows from the foregoing interpretation of the hydrogen-like spectra accomplished with its help. The correct extension of the theory, which could not afford to pass over a fact known for such a length of time as the doublet structure, was for a long time sought in vain. The splitting of the terms, which is required for the formation of the doublet structure of the alkali-metal spectra for all of the terms with the exception of the s term, demands an explanation of how, for any given quantum numbers n and k , two closely lying energy values could be produced. The assumption of an angular momentum for the atomic nucleus first suggested itself, through which the energy of the electron appeared to be different according to its sense with respect to a non-rotating nucleus. This attempt was not in accord with various experimental results, however, and proved to be incapable of execution. One of the opposing reasons is the fact that the atomic core of the alkali metal without its emission electron, that is, the alkali-metal ion, is experimentally diamagnetic like the preceding rare gas, which possesses the same electronic arrangement. If the angular momentum of the nucleus exerted an influence on the emission electron, the atomic core would have to possess a magnetic moment. Since this is not the case, this explanation, which calls on the nucleus for help, breaks down. Consequently, it became necessary to ascribe an angular momentum to the emission electron itself. Thereby the classical description of the electron, which — as an extreme generalization — regarded it simply as a point charge whose state is

fully described by the co-ordinates of space and time, was relinquished. From now on it became just as necessary to give consideration to the "nature" or "structure" of an electron as to the structure of the atomic nucleus. The acceptance of an intrinsic angular momentum or *spin*¹⁷ was only the first step. In desiring to support this with a mechanical meaning, one had accordingly to deal with an electron rather like a sphere with uniform surface charge rotating about a diameter. This picture suffices for many purposes, including those which will come under consideration here. For the explanation of other phenomena, it is however too crude and must be replaced by other quantum-mechanical concepts, upon which science is still working. The existence of an electronic spin is not only demonstrated by the doublet structure of the spectral lines, but also by other direct experimental proofs which will be brought up for discussion later (p. 261 ff).

These proofs and also others show that in an inhomogeneous field the angular momentum or spin of an electron, like the orbital momentum, can only take up absolutely fixed directions in space. The reason for this *quantization of direction* is to be sought in the restrictions prescribed by the quantum theory, which permit only discrete energy values for a rotator. Hence the angular momentum of the electron can assume only a limited number of directions in space relative to the direction of the orbital momentum, just as the orbital momentum is restricted with respect to the preferential direction of the inhomogeneous field in space. The number of these latter directions is given by the azimuthal quantum number and is equal to $2k + 1$ (concerning this see the STERN-GERLACH experiment discussed subsequently). Hence, corresponding to the spin s , $2s + 1$ directions and therefore also $2s + 1$ components are to be assumed for the alkali metals.

Now experience shows that the lines of the alkali metals are doublets, that is, the number of components is equal to 2, with the exception of the s term which is single. Thus here $2s + 1 = 2$, or $s = \frac{1}{2}$. The direction of spin can be either the same or opposed (parallel or antiparallel) to that of the orbital momentum, since, from the requirements of the quantum theory, only these two orientations are possible. The individual angular momentum of the electron and the orbital momentum are thus summed in the one case, and the former subtracted from the latter in the other.

An important deduction can now be made from the fact that with the s term, and only with this, splitting does *not* occur. In this case, one of the two possible combinations of spin and orbital momentum must accordingly drop out. Since only those momentum values have a physical meaning which are either positive or, in the limiting case, zero, the double value of the total momentum will be reduced to a single value only if the mathematical operation employed in the calculation yields a negative figure for one of the two momentum values. But, since the quantum numbers are

¹⁷ This picture originated with G. E. UHLENBECK and S. GOUDSMIT, *Naturwissenschaften*, 1925, 13, 953.

whole numbers, this is only possible when for the s term the orbital-momentum quantum number l is equal to 0.

It is thus not possible to put the orbital-momentum quantum number k in the ground state equal to the principal quantum number $n = 1$, as the BOHR model requires. Rather, in place of k the number smaller by unity, namely $l = k - 1$, must be inserted. Frequently the orbital-momentum quantum number l and the spin quantum number s are included together in a new *total angular-momentum quantum number*, also termed *inner quantum number*, $j = l \pm \frac{1}{2}$. However, as follows from its definition, this is a derived and not a new independent quantum number.

In detail, the various quantum numbers for the individual terms are as follows:

	n	l	$j_1 = l + \frac{1}{2}$	$j_2 = l - \frac{1}{2}$
s term	1	0	$\frac{1}{2}$	meaningless
p term	2	1	$\frac{3}{2}$	$\frac{1}{2}$
d term	3	2	$\frac{5}{2}$	$\frac{3}{2}$
f term	4	3	$\frac{7}{2}$	$\frac{5}{2}$

Not only can the doublet structure of the spectral lines of the alkali metals be explained by the introduction of an electronic spin, but also the fine structure of the lines and the multiplet structure appearing in other spectra, for example those of the alkaline-earth metals. Yet the three quantum numbers n , l and s or j are not sufficient for the description of the state of the electron. Among other things, this becomes apparent with the splitting of the lines in the ZEE MAN effect, which sets in in a magnetic field. It thus proves necessary to introduce a fourth quantum number which, because it makes itself noticeable with the action of a magnetic field, is named the *magnetic quantum number* and is abbreviated to m .

In order to understand the magnetic quantum number, introduced here from the experimental standpoint, it is necessary to glance briefly at the theory of magnetism. At the same time, proofs can be given for the existence of the electronic spin to supplement the considerations put forward in this section. In dealing with the magnetic theory, it is desirable essentially to limit ourselves here to the qualitative aspect, in order to be able to emphasize clearly the physical manner of thinking. The quantitative side will be made good later in the section on magnetic measurements in Chapter V (p. 378 ff).

3. Magnetism

(i) Magnetic Theories

Since the experiments of ØRSTED (1820), it has been known that a close relationship exists between electricity and magnetism. A conductor carrying a current generates a magnetic field. The movement of a conductor within a magnetic field gives rise to an electric current.

It seemed obvious to utilize these experimental results to explain

the magnetic properties of matter. The first hypothesis of this kind was enunciated as early as 1825 by AMPÈRE. AMPÈRE assumed that in ferromagnetic substances molecular currents circulate which, while normally arranged hap-hazardly in space, are orientated by a magnetic field. With this hypothesis, it is also possible to explain paramagnetism discovered by FARADAY in 1842, and, as WEBER was able to show in 1852, diamagnetism likewise (p. 381). However, it was possible to extend the AMPÈRE-WEBER hypothesis to a theory which permitted the observations to be quantitatively understood only after the electron had become known as a component part of matter. The extension of the hypothesis to the magnetic theory, which extension was based on the electronic theory, was realized by LANGEVIN in 1905.

LANGEVIN's theory replaced AMPÈRE's hypothetical molecular currents by electrons moving in closed orbits. In the simplest but at the same time most specialized case, the orbit is circular. An electron moving in a circle generates a magnetic field exactly as does a current flowing in a closed conductor, the strength of the current being measured by its magnetic moment. This can be readily calculated if one accepts the charge and mass of the electron as given, and also the radius of the electronic orbit (pp. 381—382). The sense in which the electron revolves determines the direction of the moment.

The substitution of the molecular current by the revolving motion of a small particle endowed with charge and mass leads, since one is no longer considering an electric phenomenon in a certain degree detached from matter, namely the molecular current, to a fundamentally important conclusion. *An elementary magnet of the described sort must, in addition to the magnetic moment, also possess a mechanical moment.* In consequence, it must be possible by appropriate mechanical motion to magnetize a magnetizable body; and conversely, it must be possible by magnetization to set in motion a body suspended so as to be movable in a suitable manner. An orientation of the molecular magnets consisting of revolving electrons is linked to an orientation of the revolving electronic masses. Since the molecular magnets are fixed to the whole body, the total mass of the latter thus experiences a torsional moment. Conversely, the rotation of the body must have as an outcome a certain ordering of the molecular magnets it contains, since on rotation a mechanical moment of rotation is imparted to these on account of their mass. Their orientation must lead to magnetization of the body. To be sure, these effects can be only very slight on account of the minuteness of the mass of the electrons. They can however be demonstrated. The rotation of a paramagnetic body on switching a magnetic field on and off, and the reversal of magnetism in a periodically changing magnetic field were first observed by EINSTEIN and DE HAAS¹⁸ in the year 1914. A little later, in 1915, the magnetization of a ferromagnetic body through rotation was

¹⁸ A. EINSTEIN and W. J. DE HAAS, *Verh. deut. physik. Ges.*, 1915, 17, 152.

observed by BARNETT¹⁹. Qualitatively speaking, these experiments indicate unequivocally that, with the magnetism of matter, magnetic and mechanical moments are positively coupled with one another.

Nevertheless, these experiments cannot be put forward as they stand as a proof of the LANGEVIN theory of magnetism. In addition, the magnitude of these so-called *gyromagnetic effects* must be quantitatively apparent from the theory. But, as really precise measurements²⁰ later showed, this is not the case. The theory provides a value roughly twice as large as experiment. For the substances experimentally investigated for the gyromagnetic effect, at any rate, the LANGEVIN theory is thus unable to comprehend the origin of their magnetic behaviour. Also in other cases, in the explanation of the so-called anomalous ZEEMAN effect (p. 265), among other things, the LANGEVIN theory of revolving electrons breaks down. The fact that it rested upon classical foundations could not by any chance be held responsible for this, since it allowed of translation into the language of the quantum theory without difficulty. In this, it even led to the recognition that the magnetic moment of an atom must be an integral multiple of a unit, the *magneton*. But the numerical value of this magneton, as was shown by the gyromagnetic effects and the STERN-GERLACH experiment about to be discussed, turned out to be half as large as was required. The experimental facts thereby enforced a remodelling of the LANGEVIN theory. This is best made evident from the results of the deflection of atomic beams in an inhomogeneous magnetic field in the STERN-GERLACH experiment.

(ii) The STERN-GERLACH Experiment: the Splitting of Atomic Beams in an Inhomogeneous Magnetic Field

The study of the action of a magnetic field on beams of atoms offers, for the theoretical treatment, an advantage over experiments on compact masses, this arising from the fact that the action on isolated atoms is here being dealt with. The simplest theoretical example is provided by a beam of atomic hydrogen, since here the atom consists only of a nucleus, namely a proton, and an electron. Moreover, comparison with a simple atomic model is possible, for which the interaction with the field can be calculated without difficulty. The experiment has also been carried out by STERN and GERLACH²¹ with beams of other atoms, and has led to the determination of the magnetic moment of various atoms. These results, which will come under discussion in the section on magnetic measurements in Chapter V (p. 378), will not be gone into here. In order to understand the principle underlying the experiment and its fundamental results, the example of the

¹⁹ S. J. BARNETT, *Phys. Rev.*, 1915, [ii], 6, 171; 239.

²⁰ S. J. BARNETT, *Physik. Z.*, 1934, 35, 203. See pp. 382—383.

²¹ W. GERLACH and O. STERN, *Ann. Physik*, 1924, [iv], 74, 673. Comprehensive presentation: R. G. J. FRASER, *Molecular Rays*, (Cambridge, 1931). More recent studies: W. H. BESSEY and O. C. SIMPSON, *Chem. Rev.*, 1942, 30, 239.

hydrogen atom will suffice. Generally speaking, the action of a magnetic field upon an atom is only to be reckoned with if the atom possesses a magnetic moment, that is to say, if it is a "magnetic dipole". This is the case with the hydrogen atom, which is therefore a suitable subject for experiment.

A homogeneous magnetic field effects only a moment of rotation with a magnetic dipole. Only in an inhomogeneous magnetic field does a deflecting force on a moving magnetic dipole come into play. For a suitable configuration of the dipole, in consequence of the inhomogeneity of the field, one pole is more strongly attracted than the other. According to the classical theory, the force exerted on a beam of atoms consisting of magnetic dipoles could assume a continuous series of varying values, according to the direction the magnetic vector of the atom possessed relative to the field. The result would be a simple broadening of the atomic beam. This, however, does not occur.

Instead, discrete beams of atoms are observed into which the original beam is split up. The original beam is *not* preserved. In the experiment with unexcited atomic hydrogen, *two* beams appear which are symmetrically deflected from the original direction. The deflecting force thus possesses *discrete* values. This eventuality arises through the fact that the magnetic moment of the atom can orientate itself only in certain directions with respect to an operating magnetic field force. The orientation in the field is thus *quantized*. In consequence of this *quantization of direction*, not all the desired positions are stable, but only a small definite number. In the case of unexcited atomic hydrogen, there are two such positions.

Now this dual possibility of orientation is incompatible with BOHR's model of the hydrogen atom, in which an electron revolves round the hydrogen nucleus. In point of fact, this model requires three orientations. Thus, although the theory based on the model cannot be correct, it is worth following up the idea, since thereby the meaning of the magnetic quantum number (which in reality takes no part in the experiment with atomic hydrogen, since it is equal to zero) becomes apparent.

The magnetic moment of BOHR's hydrogen atom arises from the fact that the electron revolves about the nucleus. A magnetic *orbital* moment is thus under consideration. The orbit is fixed by the principal quantum number n and the azimuthal quantum number k . For the unexcited atom, $n = k = 1$, corresponding to a circular orbit. According to its magnitude, the magnetic orbital moment is determined by the azimuthal quantum number k governing the shape of the orbit, and consequently by a quantum number m connected with this. The latter is not merely identical with k , since k does not include the direction. This is contained in the magnetic orbital moment as a vector quantity, and must be expressed by a prefixed $+$ or $-$. But in no case can the absolute value of the magnetic quantum number exceed that of k , since higher magnetic quantum numbers yield single magnetic moments which correspond to higher azimuthal quantum

numbers. The magnetic quantum number is thus limited by the restriction

$$-k \leq m \leq +k.$$

Consequently, for the unexcited hydrogen atom it can assume only the values $m = +1, 0$ and -1 . These three values would correspond to three discrete orientations of the orbital plane of the electron in a magnetic field. Of these, one, namely that corresponding to $m = 0$, would be such that the magnetic field would exert no force on the moving atom. According to this, a fraction of the atoms would perforce remain undeflected, so that, in addition to the two deflected beams, the original beam would be observed. This is however not the case. The magnitude of the observed deflection assuredly agrees with theory. The latter yields for the magnetic moment of the hydrogen atom a value of *one* BOHR magneton or, in universal constants, the value

$$\mu_0 = \frac{eh}{4\pi m_0 c} = 5584 \text{ g } \frac{1}{2} \text{ cm } \frac{5}{2} \text{ sec}^{-1}$$

(where e is the charge and m_0 the rest mass of the electron). The quantization has thus been correctly carried out, but the model employed must be wrong.

The electron of the hydrogen atom can thus not move in a closed orbit about the nucleus. Other observations and also theoretical considerations have likewise led to this conclusion, and from thence to a recognition of the fact that that which was formerly called the radius of the orbit is the distance of the electron from the nucleus at which it is most frequently to be encountered. In this, all the directions in space are equivalent, so that the hydrogen atom possesses *spherical symmetry* and not, as according to BOHR, circular symmetry.

Since, however, as demonstrated by the deflection of the atomic beam, hydrogen possesses a magnetic moment, this must arise through the electron's own rotation, if indeed magnetism is at all to be assumed as generated by the movement of electric charge. For this it is necessary, as already depicted (p. 258), to regard the electron as a body extended in space, with the charge situated on its surface. For the rotation of such a structure only two possibilities are available for the ground state of the hydrogen atom, according to whether the electron rotates towards the right or towards the left (that is, possesses a right-hand or left-hand spin). Accordingly, in a magnetic field only two configurations can occur, and the atoms in an atomic beam whose electrons have a right-hand or left-hand spin will be deflected in opposite directions by an inhomogeneous magnetic field. The different configurations and respective deflections correspond, as shown by the value found for the BOHR magneton, to a difference of 1 in the spin quantum number. Consequently it can also be said that the spin quantum number s of the individual atom is $\frac{1}{2}$, and, moreover, according to the sense of the rotation, $+\frac{1}{2}$ or $-\frac{1}{2}$.

The STERN-GERLACH experiment thus leads directly to the concept of electronic spin. For the unexcited hydrogen atom it demonstrates that no electron orbit is present, since the quantum number $k = 1$ which gives expression to such does not exist, but rather that its place is to be taken by the orbital-momentum quantum number $l = 0$, and therewith also $m = 0$ as the only value for the magnetic quantum number. However, the creation of a magnetic moment by the motion of an electron is in general by no means, excluded thereby. In other cases, in addition to the spin moment, an orbital moment whose magnitude is given by the magnetic quantum number m_l may be present, this being connected with the orbital-momentum quantum number (as indicated by the subscript l). For the same reason as explained previously with regard to the connection with the azimuthal quantum number, the restriction $-l \leq m_l \leq +l$ must hold here. The number of orientations in an inhomogeneous field, being fixed by the orbital moment, is therefore $2l + 1$ (cf. p. 258), since for m_l the value 0, as well as positive and negative values, comes into consideration. The same number must be expected for the term splitting of an atom with the orbital-momentum quantum number l by a magnetic field.

With this, the meaning of the magnetic quantum number m_l now shows itself in a clearer light than was previously the case. As long as the atom is not subjected to a magnetic field, all electrons with the same orbital-momentum quantum number l have the same energy. Their states are, as one is accustomed to saying for states of the same energy, *degenerate*. In spite of this equality in energy, the states of the various electrons with the same quantum number l are not the same. This becomes apparent when a magnetic field is applied, towards which the individual electrons behave differently, and in which they as a consequence obtain different energies. The degenerate state becomes "split". The magnetic quantum number, which is characteristic for each electron, determines the behaviour of the latter in a magnetic field, and is decisive for the magnetic orbital moment.

If orbital momentum and spin are simultaneously present, they mutually influence one another, that is to say, they are coupled. The behaviour of the atom in a magnetic field is then determined by both. Further concerning this will be found in the section on magnetic measurements (p. 381 ff).

(iii) The ZEEMAN Effect

The splitting of spectral lines in a magnetic field has its origin, in the most general case, in the interaction of the field with the electronic spin and orbital momentum. From this follows then necessity for introducing a magnetic quantum number as well as a spin quantum number. Although the leading considerations are not to be quantitatively repeated and mathematically evaluated here, at least the essentials concerning these phenomena,

which for reasons already mentioned have become so important for the development of the quantum theory of the atom, will be given.

The influence of the magnetic field on spectral lines, which FARADAY had already suspected, but with his modest experimental aids had not been able to prove, was discovered by ZEEMAN in 1896, and later named after him the ZEEMAN effect. At first it seemed to consist of a broadening of the lines. It later became apparent that the lines were split. According to the nature of the observed lines, simpler or more complicated splitting patterns were obtained. A *single* spectral line yields a symmetrical splitting into two components, whereas the original line simultaneously continues to remain visible²². This is the *normal ZEEMAN effect*. Doublets or multiplets, on the other hand, undergo a more extensive and essentially more complicated splitting in the so-called *anomalous ZEEMAN effect*. In the latter case, as is mentioned only in passing here, the application of a very strong magnetic field provides a picture which is outwardly similar to the normal ZEEMAN effect. One then sees when observing perpendicular to the magnetic field *three* blurred components, one of them in the middle between the original multiplets, and two situated symmetrically on the right and left of it. This is the so-called PASCHEN-BACK effect. It is absent as long as the magnetic field is so weak that nothing is changed with respect to the vectors of the *total* momentum, *total* spin and *total* orbital momentum²³ of the emitting atom. Within this region of field strength the real ZEEMAN effect occurs. With this, the splitting of the lines does not depend on the principal quantum number, as is shown by the similar kind of magnetic splitting of all series of the same atom. The splitting is therefore especially suitable for learning something about the magnetic and spin quantum numbers.

The normal ZEEMAN effect is susceptible to the simple interpretation on the basis of the electronic theory which H. A. LORENTZ had already given with the help of the classical concept, and which also allows itself to be formulated without difficulty in terms of the quantum theory. For single lines the electronic spin plays no part, and the splitting can consequently be calculated with the assumption that the magnetic field acts upon an electron revolving in an orbit. In this way, only the magnetic quantum number m_l appears in the quantum-theoretical presentation.

Doublets and multiplets, which owe their existence to the presence of a spin, are by contrast much less obviously split in the anomalous ZEEMAN effect. Where only the spin plays a rôle in the formation of the doublet structure, as in the doublets of the alkali metals, the kind of splitting is still fairly clear: where, however, the spin and orbital momentum coupled together determine the magnetic properties of an atom, it becomes very complicated. Yet, basically, no difficulties are created for the quantum theory of

²² The polarization phenomena of the lines are here disregarded.

²³ In the PASCHEN-BACK effect, it is no longer the *total* values of the said vectors which are coupled, but the individual components considered separately.

the effect on this account. The place of the quantum number m_l must now be taken by a new quantum number and a factor, in which the individual quantum numbers and the kind of coupling of orbital momentum and spin are included. This need not be further amplified here.

Although the theory of the ZEEMAN effect has been very thoroughly elaborated and there exists a far-reaching agreement between theory and experiment, it is nevertheless not perfectly satisfying in all details. This will not be suppressed here, although the differences which still exist appear to be without material consequence for the problems in the present treatise. The theory of the ZEEMAN effect indicates that the concept of the electron here introduced, according to which it is figuratively represented by a spatially extended, rotating electric charge, must be still further refined.

4. Spectra with Two Emission Electrons.

The Helium Spectrum, Orthohelium and Parahelium

We have so far been satisfied with considering the hydrogen-like spectra, which are given by the states and transitions of a single emission electron. These states are in turn described by the four quantum numbers. An essentially new situation arises when several emission electrons take part in the production of the spectrum, for then each emission electron cannot be regarded as characterized as to its state by any choice of quantum numbers without further considerations. The essential point of such a limitation in the choice of quantum numbers of several electrons can already be inferred from an examination of the simplest spectrum with two emission electrons, namely the *helium spectrum*.

Characteristic for the spectra of elements with two emission electrons is a number of series — principal series, first and second subordinate series, BERGMANN series — with sequences of *singlet* terms, S , P , D and F , and a corresponding system of series with a sequence of triplet terms, s , p , d and f . Of the latter, the s term is admittedly single as for the alkali metals, and for the same reason. In general²⁴, term systems combine only among themselves, that is, the electronic jumps associated with light emission occur only between energy levels of the singlet terms denoted by capital letters, or between energy levels of the triplet terms denoted by small letters, whereupon the two said systems result.

On comparison of the two systems, a peculiarity is observed which takes us essentially beyond the knowledge gained from the spectra with one emission electron. At a first glance, the line series produced by the two term systems appear to be of such a different nature, that it might be imagined that two completely different spectra having nothing to do with one another

²⁴ There are exceptions. An example of a "forbidden" line is the characteristic blue arc line of magnesium at 4571 Å. It corresponds to the transition $3^3P_1 \rightarrow 3^1S_0$. (For the term symbolism, see p. 274).

were being dealt with. On account of its spectrum, helium was thus originally taken for a mixture of two gases which were distinguished as *parahelium* with the singlet spectrum and *orthohelium* with the triplet spectrum. The spectra of the alkaline-earth metals²⁵ have a similar appearance, yet with these spectra, which on the whole are more complicated, the difference is not so striking as for the relatively simple helium spectrum.

Parahelium supplies the following series with single lines:

principal series	$\left\{ \begin{array}{l} 1S - mP \\ 2S - mP \end{array} \right.$	$(m = 2, 3 \dots)$
2nd subordinate series	$2P - mS$	$(m = 3, 4 \dots)$
1st subordinate series .	$2P - mD$	$(m = 3, 4 \dots)$
BERGMANN series	$3D - mF$	$(m = 4, 5 \dots)$

With *orthohelium* the series scheme for the triplets appears as follows:

principal series	$2s - mp_i$	$(m = 2, 3 \dots; i = 1, 2, 3)$
2nd subordinate series	$2p_i - ms$	$(m = 3, 4 \dots; i = 1, 2, 3)$
1st subordinate series.	$2p_i - md_*$	$(m = 3, 4 \dots; i = 1, 2, 3)$
BERGMANN series	$3d_* - mf_*$	$(m = 4, 5 \dots)$

The *p* terms are threefold, which is expressed by the subscript *i* and is included in the survey. The multiplicity of the *d* and *f* terms is indicated by an asterisk, but for the sake of simplicity is omitted in detail from the survey.

Apart from the difference which exists in the multiplicity of the terms for orthohelium and the singleness of the terms for parahelium, there is a still more significant difference to note in the series scheme. *With orthohelium there is no series which reverts to the 1s term:* the principal series begins in this case with the *2s* term. For a long time the line series corresponding to the *1S* term was likewise not observed for parahelium. The long-known principal series of parahelium could therefore not be represented with a *1S* term as the ground state, since the energy level corresponding to the term for the line series lay much too high for the ground state of helium, and had therefore to be written as the *2S* term. But later the principal series with the *1S* term was found in the extreme ultra-violet. For orthohelium, however, all search for such proved to be completely fruitless. It is therefore to be regarded as perfectly certain that in this case a line series with the *1s* term does not exist. This means that orthohelium can never be found in an energy-poor ground state whose energy level lies near to that of the ground state of parahelium. In other words, with helium there is only one ground state²⁶ which is relatively far removed energetically from the excited states of the helium atom, and *not* two energetically close ground states which might be denoted as a "split ground state"²⁷.

This single ground state of helium, which operates in the spectrum of

²⁵ Here the spectra observed for *atoms* of the alkaline-earth metals are intended.

²⁶ Calculation of the energy terms of the helium ground state and of orthohelium: E. A. HYLLERAAS, *Physik. Z.*, 1929, **30**, 249; *Z. Physik*, 1929, **54**, 347.

²⁷ Something of this kind occurs in the nitric oxide molecule. Cf. p. 394.

parahelium only, is characterized by the quantum numbers of the two emission electrons. These characteristic numbers must be the following (in the symbols the two electrons are distinguished by the numbers included in brackets to the right of and above the quantum numbers):

The state of the first electron is characterized by the principal quantum number $n^{(1)} = 1$, the subsidiary (orbital-momentum) quantum number $l^{(1)} = 0$, the accompanying magnetic quantum number $m^{(1)} = 0$, and further the spin quantum number $m_s^{(1)} = +\frac{1}{2}$. Correspondingly, for the second electron $n^{(2)} = 1$, $l^{(2)} = 0$, $m_l^{(2)} = 0$ and $m_s^{(2)} = -\frac{1}{2}$. This is the ground state to which parahelium returns when it emits the principal series $1S - mP$. The interchange of the two electrons yields no new state, since for the height of the energy level it is immaterial which of the two electrons has the spin quantum number $m_s = +\frac{1}{2}$ and which $m_s = -\frac{1}{2}$.

In addition to this ground state in which the two electrons have opposed spins, one might imagine a second state as existing, and differentiated from it only in that the electrons here possess the same spin, that is, $m_s^{(1)} = +\frac{1}{2}$ and $m_s^{(2)} = +\frac{1}{2}$. In this case the two emission electrons would no longer be distinguishable, since they would agree in all their quantum numbers. The non-existence of a $1s$ term shows that such a state of affairs does not occur. Behind this fact there lies a universal law, the cause of which is not known, but which perhaps can be formulated as the following heuristic principle:

In no atom can two or more electrons be present which agree in all four quantum numbers.

This is the PAULI principle²⁸, which may also be more completely named the PAULI exclusion principle. According to this, the quantum numbers for several electrons can thus not be chosen at will, but are subject to the limitation that, through their four quantum numbers, the electrons must remain distinguishable from one another.

The PAULI principle has so far proved itself valid in all cases. In order to provide another example of spectra with two emission electrons, it might be mentioned that for the alkaline earths the triplet principal series, as for orthohelium, proceeds from the excited $2s$ state, there being no $1s$ state. Here, in the case of magnesium, the principal quantum number $n = 3$ for both emission electrons, the subsidiary quantum number $l = 0$, the magnetic quantum number $m_l = 0$, while the spin quantum number is again differentiated by $m_s^{(1)} = +\frac{1}{2}$ and $m_s^{(2)} = -\frac{1}{2}$.

5. Atomic Structure and the PAULI Exclusion Principle

The PAULI principle in conjunction with certain rules concerning the four quantum numbers of an electron enables the structure of the electronic envelope of the atoms to be derived. It is accordingly possible to specify in which states, characterized by quantum numbers, the individual

²⁸ W. PAULI, *Z. Physik*, 1925, **31**, 765.

electrons of an envelope containing a known number of electrons might be found. *A derivation of the periodic regularities which receive expression in the Periodic System is thereby provided.*

For the four quantum numbers, by which an electron is characterized, a simple scheme can be erected based on the fact that the subsidiary quantum number l must always be smaller than any given principal quantum number n , and is linked to the magnetic quantum number m_l by the condition $-l \leq m_l \leq +l$. The spin quantum number can assume only the values $+\frac{1}{2}$ and $-\frac{1}{2}$. For any given principal quantum number, the number of possible combinations with the remaining quantum numbers can thus be stated at the outset. These combinations can be further subdivided as to detail if the subsidiary quantum number is employed in addition to the principal quantum number as ordering principle.

shell	n	l	m_l	m_s	total number of electrons
K	1	0	0	$+\frac{1}{2}$ $-\frac{1}{2}$	2
L	2	0	0	$+\frac{1}{2}$ $-\frac{1}{2}$	8
		1	0	$+\frac{1}{2}$ $-\frac{1}{2}$	
			+1	$+\frac{1}{2}$ $-\frac{1}{2}$	
			-1	$+\frac{1}{2}$ $-\frac{1}{2}$	
				$+\frac{1}{2}$ $-\frac{1}{2}$	
M	3	0	0	$+\frac{1}{2}$ $-\frac{1}{2}$	18
		1	0	$+\frac{1}{2}$ $-\frac{1}{2}$	
			+1	$+\frac{1}{2}$ $-\frac{1}{2}$	
			-1	$+\frac{1}{2}$ $-\frac{1}{2}$	
		2	0	$+\frac{1}{2}$ $-\frac{1}{2}$	
			+1	$+\frac{1}{2}$ $-\frac{1}{2}$	
			-1	$+\frac{1}{2}$ $-\frac{1}{2}$	
			+2	$+\frac{1}{2}$ $-\frac{1}{2}$	
			-2	$+\frac{1}{2}$ $-\frac{1}{2}$	
				$+\frac{1}{2}$ $-\frac{1}{2}$	
N	4	0	0		} 32
		1	$0, \pm 1$	$= (2 \times 3)$	
		2	$0, \pm 1, \pm 2$	$= (2 \times 5)$	
		3	$0, \pm 1, \pm 2, \pm 3$	$= (2 \times 7)$	

(each of these states being doubly occupied with $m_s = +\frac{1}{2}$ and $-\frac{1}{2}$)

Since, now, according to the PAULI principle, all the electrons of an element must be distinguishable as to their states from one another, this scheme can at the same time be employed to reproduce all the "electronic configurations" which are at all possible in the grouping of electrons about an atomic nucleus. In this it is customary to collect the electrons with the same principal quantum number into a "shell", the electrons with $n = 1$ being relegated to the K shell, those with $n = 2$ to the L shell, those with $n = 3$ to the M shell, and so on. On consideration of the subsidiary quantum numbers, subgroups arise within these shells.

It thus appears, in correspondence with the lengths of the periods, that the K shell can contain only 2 electrons, the L shell 8, the M shell 18 and the N shell 32. If the O shell could be completed, room in it for 50 electrons would be provided.

Since not more than 8 electrons can be housed in the L shell, it follows that for compound-formation with the elements of the first period never more than four atoms can be linked to an atom of one of these elements; for, with simple bonding, each link demands at least two electrons which are common to the outer shells of the linked atoms. The pronouncement of the octet rule (pp. 37, 246) is identical with this, and therefore, for the first period, theoretically established. For the higher periods it need not be valid, since already with the M shell a maximum of 18 electrons may be received into it.

The structure of the individual atoms of the elements does not yet follow from this scheme, for, on advancing with the atomic number through the Periodic System, the addition of electrons does not invariably succeed in such a way that one shell after the other is filled up. Rather, as is first noticed with potassium and calcium, electrons may also be accepted into an outer shell (here the N shell) before the inner shell (here the M shell) is completely filled. The reason for this is that the energies of the electrons entering the outer shell are less than they would be if the electrons entered the inner shell. If, then, as happens subsequently, the addition of electrons to the outer shell is not continued but addition to the inner shell recommenced, as with scandium, for which the third valence electron, and with titanium, for which the third and fourth valence electrons, are included in the M shell, the underlying reason is that the energies of these further electrons are henceforth smaller in the inner shell than in the outer. To be sure, the difference in energy is often very small, so that the electrons are easily raised to the somewhat higher energy level of the outer shell, where they are able to operate as valence electrons, or are given up with the electrons of the latter shell on ion-formation. This is why scandium is habitually trivalent and titanium preferentially tetravalent.

It can still not be theoretically calculated beforehand in which of two such closely lying states the electron has the lesser energy. The terms which belong to the electrons in the ground state must consequently be derived

experimentally from the spectrum. Only in this way can a complete knowledge be obtained of the electronic configurations of the atoms in their ground states. The configurations are given in the accompanying table. The subgroups arranged according to the subsidiary quantum numbers are identified by the term letters *s*, *p*, *d* and *f*, as used for the spectra.

6. Term Symbolism

The state of an atom is of significance for its chemical reactivity. A term symbolism has been introduced in order to be able briefly to identify the atomic state, and likewise the spectral series to which it belongs. From the

The electronic configuration of the elements in the Periodic System

<i>n</i> =	K		L		M			N		<i>n</i> =	K		L		M			N				O				P
	1	2	2	2	3	3	3	4	4		1	2	3	3	3	4	4	4	4	5	5	5	5	6		
	<i>s</i>	<i>s</i>	<i>p</i>	<i>p</i>	<i>d</i>	<i>s</i>	<i>p</i>	<i>s</i>	<i>p</i>		<i>s</i>	<i>p</i>	<i>d</i>	<i>f</i>	<i>s</i>	<i>p</i>	<i>d</i>	<i>f</i>	<i>s</i>	<i>p</i>	<i>d</i>	<i>f</i>	<i>s</i>			
1 H	1									37 Rb	2	8	18	2	6					1						
2 He	2									38 Sr	2	8	18	2	6					2						
3 Li	2	1								39 Y	2	8	18	2	6	1				2						
4 Be	2	2								40 Zr	2	8	18	2	6	2				2						
5 B	2	2	1							41 Nb	2	8	18	2	6	4				1						
6 C	2	2	2							42 Mo	2	8	18	2	6	5				1						
7 N	2	2	3							43 Tc	2	8	18	2	6	6				1						
8 O	2	2	4							44 Ru	2	8	18	2	6	7				1						
9 F	2	2	5							45 Rh	2	8	18	2	6	8				1						
10 Ne	2	2	6							46 Pd	2	8	18	2	6	10										
11 Na	2	2	6	1						47 Ag	2	8	18	2	6	10				1						
12 Mg	2	2	6	2						48 Cd	2	8	18	2	6	10				2						
13 Al	2	2	6	2	1					49 In	2	8	18	2	6	10				2	1					
14 Si	2	2	6	2	2					50 Sn	2	8	18	2	6	10				2	2					
15 P	2	2	6	2	3					51 Sb	2	8	18	2	6	10				2	3					
16 S	2	2	6	2	4					52 Te	2	8	18	2	6	10				2	4					
17 Cl	2	2	6	2	5					53 I	2	8	18	2	6	10				2	5					
18 A	2	2	6	2	6					54 Xe	2	8	18	2	6	10				2	6					
19 K	2	2	6	2	6		1			55 Cs	2	8	18	2	6	10				2	6			1		
20 Ca	2	2	6	2	6		2			56 Ba	2	8	18	2	6	10				2	6			2		
21 Sc	2	2	6	2	6	1	2			57 La	2	8	18	2	6	10				2	6	1		2		
22 Ti	2	2	6	2	6	2	2			58 Ce	2	8	18	2	6	10	1			2	6	1		2		
23 V	2	2	6	2	6	3	2			59 Pr	2	8	18	2	6	10	2			2	6	1		2		
24 Cr	2	2	6	2	6	5	1			60 Nd	2	8	18	2	6	10	4			2	6			2		
25 Mn	2	2	6	2	6	5	2			61 Pm	2	8	18	2	6	10	5			2	6			2		
26 Fe	2	2	6	2	6	6	2			62 Sm	2	8	18	2	6	10	6			2	6			2		
27 Co	2	2	6	2	6	7	2			63 Eu	2	8	18	2	6	10	7			2	6			2		
28 Ni	2	2	6	2	6	8	2			64 Gd	2	8	18	2	6	10	7			2	6	1		2		
29 Cu	2	2	6	2	6	10	1			65 Tb	2	8	18	2	6	10	8			2	6	1		2		
20 Zn	2	2	6	2	6	10	2			66 Dy	2	8	18	2	6	10	9			2	6	1		2		
31 Ga	2	2	6	2	6	10	2	1		67 Ho	2	8	18	2	6	10	10			2	6	1		2		
32 Ge	2	2	6	2	6	10	2	2		68 Er	2	8	18	2	6	10	11			2	6	1		2		
33 As	2	2	6	2	6	10	2	3		69 Tm	2	8	18	2	6	10	13			2	6			2		
34 Se	2	2	6	2	6	10	2	4		70 Yb	2	8	18	2	6	10	14			2	6			2		
35 Br	2	2	6	2	6	10	2	5		71 Lu	2	8	18	2	6	10	14			2	6	1		2		
36 Kr	2	2	6	2	6	10	2	6		72 Hf	2	8	18	2	6	10	14			2	6	2		2		

The electronic configuration of the elements in the Periodic System (continued)

$n =$	K	L	M	N	O				P			Q
	1	2	3	4	5				6			7
					<i>s</i>	<i>p</i>	<i>d</i>	<i>f</i>	<i>s</i>	<i>p</i>	<i>d</i>	<i>s</i>
73 Ta	2	8	18	32	2	6	3		2			
74 W	2	8	18	32	2	6	4		2			
75 Re	2	8	18	32	2	6	5		2			
76 Os	2	8	18	32	2	6	6		2			
77 Ir	2	8	18	32	2	6	7		2			
78 Pt	2	8	18	32	2	6	9		1			
79 Au	2	8	18	32	2	6	10		1			
80 Hg	2	8	18	32	2	6	10		2			
81 Tl	2	8	18	32	2	6	10		2	1		
82 Pb	2	8	18	32	2	6	10		2	2		
83 Bi	2	8	18	32	2	6	10		2	3		
84 Po	2	8	18	32	2	6	10		2	4		
85 At	2	8	18	32	2	6	10		2	5		
86 Rn	2	8	18	32	2	6	10		2	6		
87 Fr	2	8	18	32	2	6	10		2	6		1
88 Ra	2	8	18	32	2	6	10		2	6		2
89 Ac	2	8	18	32	2	6	10		2	6	1	2
90 Th	2	8	18	32	2	6	10		2	6	2	2
91 Pa	2	8	18	32	2	6	10		2	6	3	2
92 U*	2	8	18	32	2	6	10	3	2	6	1	2

* This configuration was recently established by C. C. KIESS, C. J. HUMPHREYS and D. D. LAUN, *J. Research National Bur. Standards, U.S.*, 1946, **37**, 57. It is not improbable that the elements immediately preceding uranium also contain *f* electrons in their O shell (but with regard to thorium, see the discussion on p. 301). The electronic configurations of the ground states of a number of other elements are not finally settled.

term symbol, when one knows how to interpret it, it is possible to extract the characteristic quantum numbers and the structure of the spectral lines (whether singlet or multiplet).

Before the symbolism can be gone into, it must be observed in advance that, with respect to the quantum numbers, it is not concerned with the quantum numbers of the individual electrons — in order to express these a complete system would in any case be necessary — but with the *resultant quantum numbers*, these being calculated from the individual quantum numbers according to certain definite rules. These are:

- the resultant orbital-momentum quantum number L ;
- the resultant spin quantum number S ;
- the resultant inner quantum number J .

The momenta belonging to these quantum numbers are:

- the total orbital momentum \vec{L} ;
- \vec{S} , the angular momentum due to the spin;
- the total angular momentum \vec{J} (arising through the combination of orbital

momentum and spin — cf. the definition of the total-momentum quantum number = inner quantum number j for a single electron, p. 259).

The quantum numbers are connected with the momenta according to the following equations (the derivation of which cannot be given here):

$$\vec{L} = h\sqrt{L(L+1)}; \quad \vec{S} = h\sqrt{S(S+1)}; \quad \vec{J} = h\sqrt{J(J+1)}.$$

The following relationships exist with the quantum numbers of the individual electrons, l_i , m_i and m_j .

The orbital momenta and the orbital-momentum quantum numbers l_i of the individual electrons add up vectorially to the values \vec{L} and L . This vector addition is admittedly different from the usual vector addition in which, according to the angle made by the vectors, any desired value lying between the algebraic sum and difference of the vectors can be assumed. The difference lies in the fact that, corresponding to the demands of the quantum theory, only integral sums may result. The consequence of such a vectorial addition is that, *e.g.*, for two electrons with the quantum numbers l_1 and l_2 ($l_1 \geq l_2$), the resultant quantum number L can be equal not only to the algebraic sum of l_1 and l_2 corresponding to vectorial addition of parallel vectors, but can also assume all integral values lying between this sum $l_1 + l_2$ and the difference $l_1 - l_2$. At its minimum value it can be equal to the difference $l_1 - l_2$, which corresponds to vectorial addition of opposed vectors.

The spin quantum number of the individual electrons ($+\frac{1}{2}$ and $-\frac{1}{2}$), by way of contrast, add up algebraically to give S , that is to say, the spins with the same sense of rotation are to be added, and those which oppose subtracted from one another.

The resultant inner quantum number J for the total angular momentum is calculated from l and m_j , since the inner quantum number j of the individual electrons is linked to l and m , by the relationship

$$j = l + \frac{1}{2} \text{ and } j = l - \frac{1}{2}.$$

On account of the restriction $l \geq 1$ for $j = l - \frac{1}{2}$ (p. 259), it can assume only positive values. For an even number of electrons, j is integral, for an uneven, half-integral.

The various values which L , S and J can assume for a definite number of electrons with prescribed quantum numbers are illustrated by a few examples.

L : 2 electrons with $l_1 = 2$, $l_2 = 1$:

$l_1 + l_2 = 3$, $l_1 - l_2 = 1$, with 2 lying in between, so that $L = 1, 2, 3$.

2 electrons with $l_1 = 3$, $l_2 = 2$:

$l_1 + l_2 = 5$, $l_1 - l_2 = 1$, with 4, 3 and 2 in between, so that $L = 1, 2, 3, 4, 5$.

3 electrons with $l_1 = 3$, $l_2 = 2$, $l_3 = 1$:

$l_1 + l_2 + l_3 = 6$, $l_1 - l_2 - l_3 = 0$, so that $L = 0, 1, 2, 3, 4, 5, 6$.

S : 2 electrons:

$$\frac{1}{2} + \frac{1}{2} = 1, \frac{1}{2} - \frac{1}{2} = 0.$$

3 electrons:

$$\frac{1}{2} + \frac{1}{2} + \frac{1}{2} = \frac{3}{2}, \frac{1}{2} + \frac{1}{2} - \frac{1}{2} = \frac{1}{2}.$$

5 electrons: $\frac{5}{2}, \frac{3}{2}, \frac{1}{2}$.

J : 2 electrons with $l_1 = 1, l_2 = 0, m_{s_1} = m_{s_2} = \frac{1}{2}$:

$$l_1 + m_{s_1} + m_{s_2} = 2, l_1 - m_{s_1} - m_{s_2} = 0, l_1 + m_{s_1} - m_{s_2} = 1.$$

The resultant quantum numbers L and J are given in the term symbols. It suffices to state only two quantum numbers, since the third (S) can be calculated from them directly. The numerical value of the quantum number L is not written down in the term symbol, but expressed by a symbol indicating the nature of the corresponding spectral series. The letters chosen for this form, as it were, the centre-piece of the symbol, having the following meaning:

S	=	term with the quantum number	$L = 0$	(“sharp” series)		
P	=	“	“	“	$L = 1$	(“principal” series)
D	=	“	“	“	$L = 2$	(“diffuse” series)
F	=	“	“	“	$L = 3$	(BERGMANN series)
G	=	“	“	“	$L = 4$	

The principal quantum number n is written in front of the symbol and on the same level (like a factor, which, however, it naturally is not). If it is equal to 1, it is usually omitted.

The resultant inner quantum number J appears as a subscript on the right of the letter characterizing the series. The number prefixed above denotes the structure of the lines:

1 = singlet, 2 = doublet, 3 = triplet, n = multiplet with n lines.

Examples: 3^3P_2 means a term belonging to a triplet and with the quantum numbers $n = 3, L = 1, J = 2$.

The following terms (each term with different quantum numbers) are determinative for the *parahelium spectrum*, which possesses only single lines: $^1S_0, ^1P_1, ^1D_2, ^1F_3$.

The terms for the *orthohelium spectrum* with its triplets are $^3S_1, ^3P_2, ^3P_1, ^3P_0$ (latter three contracted to $^3P_{2,1,0}$), $^3D_{3,2,1}, ^3F_{4,3,2}$.

Each term corresponds to a definite energy value. The energy values corresponding to the various terms can be pictorially represented in term diagrams, but these will not be reproduced here. The term of lowest energy in a series is denoted as the ground term of this series. By ground term of an atom is understood merely that term which is poorest in energy. Helium may again serve as an example. The orthohelium spectrum, since it is emitted by an excited atom, possesses no ground term. The ground terms of helium are the terms given above for the parahelium spectrum.

The ground term of lowest energy for helium is the 1S_0 term. For an S_0 term, which also occurs for other atoms, it is characteristic that all the

resultant quantum numbers L , S and J are equal to zero. For them a complete compensation of the three momenta \vec{J} (due to the angular momenta of the different electrons), \vec{L} (due to the orbital momenta) and \vec{S} (due to the spin momenta) takes place in the ground state.

In the Periodic System, atoms constructed in this way are found with the rare gases, and then again with the elements of group II. With the latter, the compensation rests upon the fact that the two valence electrons are fitted into an s subgroup on top of a shell of eight or eighteen electrons, in which subgroup, since it holds only two electrons, they must have opposed spins. For the elements of group I with a single emission electron whose spin cannot be compensated, the ground states of the atoms correspond to 2S_0 terms. In consequence of the uncompensated spin, which can have a sense of rotation towards the right or left, a splitting of the lines into doublets occurs (p. 258).

Commencing with the elements whose ground states correspond to an S_0 term, it is possible to state the ground terms of the elements immediately following without further ceremony, provided the addition of further electrons succeeds regularly on to a stable shell, as just depicted for the elements in groups I and II, or on to a completed s subgroup, but not when inner incomplete shells of electrons are being filled, as in the case of the transition elements. Such an orderly construction of a p subgroup with its six electrons on top of an s subgroup occurs for those elements standing within six places before a rare gas, since the addition of six p to two s electrons means the erection of the octet of a rare gas. This condition is fulfilled for the elements following beryllium, magnesium, zinc, cadmium and mercury. The considerations of their ground terms is of significance not only for the spectroscopist, but also for the chemist who, from the regularity in the ground terms, can infer a regularity in chemical behaviour.

The regularity in the ground terms, as also in the quantum numbers L and S , consists of a marked symmetry when they are followed on the one hand from group II and on the other from group 0, as the following table illustrates:

group	II	III	IV	V	VI	VII	0
atomic number	4	5	6	7	8	9	10
	12	13	14	15	16	17	18
	30, 48, 80	31, 49, 81	32, 50, 82	33, 51, 83	34, 52, 84	35, 53	36, 54, 86
ground terms	1S_0	$^2P_{1/2, 3/2}$	$^3P_{0, 1, 2}$	$^4S_{3/2}$	$^5P_{1, 2, 3}$	$^6P_{3/2, 5/2, 7/2}$	1S_0
	L	0	1	1	0	1	1
S	0	$\frac{1}{2}$	1	$\frac{3}{2}$	1	$\frac{1}{2}$	0
J for the lowest term	0	$\frac{1}{2}$	0	$\frac{3}{2}$	2	$\frac{3}{2}$	0

The atoms thus behave on the addition of the first p electron as on the removal of the sixth and last p electron. This rule for incomplete subgroups

(or *Lückensatz*) is due to PAULI. It can also be formulated by saying: *In the p subgroup, the occupied and unoccupied places in the first and second halves are interchanged.* For the inner quantum number J , when it is referred to the *deepest* term, there is admittedly no symmetry. Symmetry appears only when all the J values are written in without regard to the energy levels of the terms. The establishment of this rule, since it is devoid of importance for chemical deductions, can be omitted here.

It is possible for the chemist to draw various qualitative conclusions from this rule. Firstly, the elements of group VII preceding the rare gases, namely the halogens, can behave like monovalent elements with one valence electron, and the preceding elements of group VI like divalent elements with two electrons. It further follows that fundamentally the elements of group III, inasmuch as they are situated five places before a rare gas, are able to appear as monovalent, and those of group IV as divalent. A prerequisite is naturally that a sufficiently large difference exists between the energies of the s and p electrons, concerning which the table of the terms provides no information. *Experience teaches* that this is not the case in the first and second periods, where, with respect to chemical activity of the elements as far as group IV (apart from exceptional cases), the s electrons are implicated in the same way as the p electrons (p. 413). With increasing number of the period, the firmness with which the s subgroup is held increases relative to the p subgroup, so that in the series Ga, In, Tl the monovalent state, and in the series Ge, Sn, Pb the divalent state become increasingly stable, and even appear to be preferred to the tri- and tetravalent states respectively for the members with the highest atomic weight. In an exactly corresponding manner, the "rare-gas resemblance" which comes to expression in the similarity of the ground terms for the divalent elements Be, Mg, Zn, Cd and Hg increases with increasing atomic weight. This shows itself in a marked increase in volatility within the series. The higher the atomic weight of the metal, the weaker the metallic bonding provided by the two s electrons, as the following comparison of the boiling points shows:

Be 2970° Mg 1100° Zn 918° Cd 767° Hg 358°

With beryllium, whose boiling point is unusually high, the $2s$ subgroup does not exhibit any noticeable inclination to become stabilized as a rare-gas-like shell of two electrons. But already with magnesium the boiling point is rather low for a metal, noticeably lower than with calcium which boils at 1451°, whereas for the higher members of the subgroup the boiling point falls very sharply to that of mercury. The group of two s electrons is indeed still capable of metallic bonding in mercury, but the tendency to form isolated atoms like the rare gases has already become very considerable. In order to avoid misunderstanding, let it again be stated that a relatively high volatility can by all means be predicted for zinc, cadmium and mercury by reason of the terms, but that the increase in volatility within this series *cannot* be inferred from the terms.

7. Atomic Weights. Isotopy

After the discovery of the Law of Constant and Multiple Proportions, it was an important task to derive the combining weights of the elements from the stoichiometric ratios determined by analysis. They found their obvious theoretical explanation as ratios between the weights of the elementary atoms by means of the atomic theory, and were consequently named *atomic weights*. At first, as a result of the Law of Constant and Multiple Proportions, they naturally remained indeterminate by a factor expressible as a small whole number until it was possible to remove this uncertainty by the application of AVOGADRO's Hypothesis, by the utilization of the law of DULONG and PETIT, and finally also with the assistance of the Periodic System. The atomic weight of an element, the measure for the mass of its atoms, now appeared as a fundamental property characteristic of the respective element. Consequently, not only did its exact determination appear important from the standpoint of the practice of quantitative analysis, but also as significant in the extreme from the scientific standpoint. Hopes were harboured of deriving from the numerical material of the atomic weights some sort of temporarily hidden relationship between the atoms of different elements, thus taking the first step towards answering the question of how the elements known in nature, not only on the earth but also in the stars, came into existence. It was possible to devote oneself all the more readily to this hope, since in physics fundamental laws had already frequently been obtained from the correct interpretation of numerical material secured by precise observations, as for example KEPLER's laws and the laws of falling. The saying which HERMANN KOLBE had introduced in the lecture theatre of his Chemical Institute at Leipzig: *Gott hat alles nach Mass und Zahl geordnet* (God has ordered everything by measure and number), illustrates that the chemist also recognized the significance for chemistry of dimensions expressible by numbers and therefore measurable. Because of the qualitative character which the observations made on chemical reactions bore before the advance of physical chemistry, the determinations of atomic weights for a long time provided the only exact numerical measurements in chemistry besides the melting and boiling points. It is thus only natural that, with their help, attempts were made to penetrate deeper into the relationships between the various kinds of atoms. One such attempt already came about at a time when the atomic-weight determinations still left much to be desired in precision, and that too on the basis of a hypothetical speculation. In the year 1816, the English physician PROUT put forward the hypothesis that all atomic weights were multiples of the atomic weight of hydrogen; if the latter was put equal to unity, all atomic weights would have to become whole numbers. In addition, DALTON had likewise by that time derived only integral atomic weights relative to hydrogen from his very inexact measurements. PROUT's hypothesis was not based on a critical

sifting of the available numerical data, but sprang from the philosophical need to be able to regard all matter as built up from an original material. For the correctness of his assertion, PROUT was then able to cite actually only the atomic weights of carbon²⁹, nitrogen, oxygen and sulphur. Of the remaining elements, then numbering about fifty, the atomic weights were too inaccurately known to be able to serve as a test of PROUT's hypothesis. Nevertheless, it was sufficiently striking that the proportions by weight of hydrogen to oxygen in water were very exactly 1 : 8, of hydrogen to nitrogen in ammonia 3 : 14, of oxygen to sulphur in sulphur dioxide 1 : 1, and of oxygen to carbon in carbon monoxide 4 : 3. Thus, in spite of, or rather precisely because of its inadequate experimental foundation, PROUT's hypothesis exerted a very stimulating influence on research. As some of the atomic-weight determinations of the most exact analyst of that time, namely BERZELIUS, were already in contradiction with it, it invited a conscientious testing and was the cause of a large number of atomic-weight determinations, thus not only bringing about an exact knowledge of atomic weights, but considerably extending the practice of analytical chemistry. Apart from BERZELIUS, who very soon believed he had disposed of PROUT's hypothesis in the negative sense, the question was taken up in particular by DUMAS, who caused STAS to begin his masterly series of experiments on the determination of atomic weights. STAS was very soon able to prove, in agreement with BERZELIUS, that the atomic weight of chlorine, which can be determined very exactly by a variety of methods, is not a whole number when referred to hydrogen, but bears the rounded value 35.5.

Since yet other atomic weights also came to be known with certainty as non-integral, the hypothesis of PROUT appeared to be dispensed with. Notwithstanding, attempts were made to rescue it, and, in consideration firstly of the atomic weight of 35.5 found for chlorine, it was next assumed that a multiple of half of the atomic weight of hydrogen was also admissible. However, if it was desired to remain in harmony with observation, it was soon seen to be necessary to allow a quarter. Because of these attempts at rescue, the hypothesis was so discredited, that it was finally rejected by all serious-minded scientists.

It would have been more correct if the basic idea had been retained, and from this demonstrated that many atomic weights nevertheless come strikingly near to whole numbers. Later, when most atomic weights could be determined really precisely, that is, to within about 0.1 or 0.2 units, it was admittedly remarked upon from various quarters that many more atomic weights lie very close to whole numbers than corresponds to probability. Today, now that the accuracy of the atomic-weight determinations is in most cases materially greater than 0.1 of a unit, it is possible to make per-

²⁹ Moreover, in the eighteen twenties an atomic weight for carbon of about 12.15 — with respect to O = 16 — which rested upon an inaccurate determination by BERZELIUS was in use, instead of the correct, almost exactly integral value 12.01.

fectly reliable statements about the matter. Of 84 precisely determined atomic weights, 20, or about a quarter, are removed by not more than 0.05 from whole numbers. If a deviation of 0.1 units is allowed, about 20 further elements are added, so that about half of the elements have atomic weights which are integral to within a precision of 0.1. According to probability, an approach of the atomic weight to within 0.05 of a whole number is to be expected for a tenth, and to within 0.1 for a fifth of all the elements. From this it appears, though not for all elements, yet for a considerable fraction, that a grain of truth is contained in PROUT's hypothesis.

With the atomic weights it thus appeared on the whole as if, on top of a broad general conformity to the rule, some sort of influence was superimposed which veiled it. The same impression was obtained from the Periodic System. This was erected on the basis of atomic weights as the ordering principle, which principle was nevertheless incomprehensibly broken in a few places. At the time the Periodic System was drawn up, the most striking exception was the placing of tellurium and iodine, since tellurium, which indubitably belongs to group VI, has a higher atomic weight than iodine, which equally certainly belongs to group VII. Less noticeable was the placing of cobalt with atomic weight 59.0 before nickel with atomic weight 58.7. Later, after the discovery of the rare gases, these instances were joined by a further very striking exception, the argon-potassium pair. In more recent times, the case of thorium (atomic weight 232.12) in group IV and protactinium (atomic weight 230.6³⁰) in group V of the Periodic System has become known. Apart from the last-named example, the irregularities were the cause of numerous fresh determinations of the atomic weights, which, however, only served to confirm the exceptions. Rare as the exceptions were, they nevertheless showed that the ultimate ordering principle of the Periodic System had not been found in the atomic weights, and that the magnitude of the atomic weights was dependent in individual cases on certain "chance" influences which had nothing to do with the position in the System.

The belief that atomic weights constituted a fundamental property of the chemical elements was however first seriously shaken when radioactive transmutations brought acquaintance with numerous new radioactive elements, for which there was no room in the Periodic System. There were elements which, by reason of their markedly different half-life periods, were without doubt different, even though chemically identical in behaviour, like, for example, uranium I with a half-life of 4.6×10^9 years and uranium II with one of 10^6 years, or radium, an α -emitter of 1580 years, and mesothorium I, a β -emitter of 6.7 years. On account of their like chemical

³⁰ A. VON GROSSE, *Proc. Roy. Soc.*, 1935, A 150, 363. The limits of error for this determination, in comparison with the other atomic weights, is quite considerable, namely ± 0.5 . Further articles concerning protactinium: *J. Am. Chem. Soc.*, 1934, 56, 2200; *Ind. Eng. Chem.*, 1935, 27, 422; *Ann. Rep. Chem. Soc.*, 1935, 32, 143 ff.

behaviour, such elements had to be relegated to the same group of the Periodic System, in the quoted examples uranium I and II to group VI, and radium and mesothorium I to group II. At the same time, these elements inescapably possessed different atomic weights, although they fell into the same positions in the Periodic System. Certainly, this could not be demonstrated by direct atomic-weight determinations, but could be derived with certainty from the atomic weights of the initial elements and the number of emissions of α -particles of mass 4 taking place in their transmutation to the new elements. Thus, for example, between U_I and U_{II} is one α emission (in addition to two β emissions); since the atomic weight of U_I is 238, that of U_{II} must be 234. Mesothorium originates from thorium of atomic weight 232 by one α emission and must therefore have the atomic weight 228. Radium, on the other hand, as has been found by direct atomic-weight determination, has the atomic weight 226. Such elements, which occupy the same position in the Periodic System, but are distinguished by their half-life periods and in general also by their atomic weights³¹, are called, according to SODDY (1909), *isotopes*³².

As is learnt by a glance at the non-radioactive end products of the radioactive series, isotopy is not limited to the radioactive elements; but it can be especially easily detected with the latter through the characteristic half-life periods, whereas in other cases precise determinations of the atomic weights must be carried out. The decay series end up with lead³³, the uranium series moreover with uranium lead (RaG) after eight α emissions, the thorium series with thorium lead (ThD) after six α emissions, and the actinium series with actinium lead (AcD) after six α emissions (reckoned from protactinium). From the atomic weights of U (238), Th (232) and Pa (231), the rounded atomic weights 206, 208 and 207³⁴ follow successively for the different "sorts" of lead. A direct measurement was possible for uranium lead and thorium lead, which respectively occur in sufficient quantities in aged thorium-free uranium minerals and uranium-free thorium minerals otherwise containing from the time of their formation no noteworthy quantities of ordinary lead. Independently of each other, HÖNIGSCHMID³⁵ and RICHARDS³⁶ conducted atomic-weight determinations on lead from such

³¹ It happens on very rare occasions that two radioactive isotopes have the same atomic weight and are only to be differentiated by their half-life periods, like the two β -emitters UX_2 (1.14 min) and UZ (6.7 hours) of atomic weight 234 resulting from UX_1 by bifurcation at a β emission. In addition, there are two artificial radioactive bromine isotopes of atomic weight 80: W. BOTHE and W. GENTNER, *Z. angew. Chem.*, 1937, 50, 600; *Naturwissenschaften*, 1937, 25, 284.

³² The existence of isotopic species of atoms was recognized almost simultaneously by F. SODDY, by D. STRÖMHOLM and T. SVEDBERG and by W. MARCKWALD in the years 1909–1910.

³³ The recently discovered neptunium series terminates with bismuth.

³⁴ In addition to these three stable isotopes of lead, four other radioactive isotopes are known: RaB (214, 26.8 min); RaD (210, 22 yr); ThB (212, 10.6 hr); AcB (211, 36 min).

³⁵ O. HÖNIGSCHMID, *Z. Elektrochem.*, 1914, 20, 319; O. HÖNIGSCHMID and S. HOROVITZ, *Sitzungsber. Akad. Wiss. Wien, Math.-nat. Kl. IIa*, 1914, 123, 2407.

³⁶ T. W. RICHARDS and C. WADSWORTH, *J. Am. Chem. Soc.*, 1916, 38, 2613.

minerals with the same results. The lead from the uranium mineral had the atomic weight 206.09, and that from the thorium mineral 207.9.

Meanwhile, soon after the existence of isotopic elements had become known, the advance in knowledge of atomic structure combined with the results of X-ray spectroscopy led in the year 1913 to the dethronement of the atomic weight with its dominating position in the Periodic System and to the insertion in its stead of the atomic number Z , which is equal to the nuclear charge of the atom. With the help of this number, as was found by MOSELEY (1913), the frequency of a particular line in the X-ray spectrum depending upon the element for which it is observed could be given by a simple function, namely MOSELEY'S Law: this states that the square root of the frequency of the line is proportional to the atomic number. With the atomic weight, no simple relationship of this kind can be produced. Isotopic elements accordingly have the same atomic number but different atomic weights. They also give the same X-ray spectrum. This and the identity of chemical behaviour was, according to BOHR'S theory of atomic structure, the result of the identical structure of the envelopes of electrons. There are also atoms with different electron envelopes but with the same mass. Such atoms are termed *isobars*. For example, the most abundant zinc isotope ^{64}Zn is isobaric with the rarest nickel isotope ^{64}Ni .

As soon as it was established that isotopy also occurred with the non-radioactive elements, the question arose whether the elements were not quite generally mixtures of isotopes, the observed atomic weights representing mean values which follow from the relative proportions of the individual isotopes of different mass. At the same time, a renewed testing of PROUT'S hypothesis was to be regarded as a further problem in the background. The deviation of the atomic weights from whole numbers could very well depend upon the fact that they were not pure elements but isotopic mixtures. The requirement that each individual isotope should be integral might very easily be fulfilled, but it does not of course need to apply for a mixture of isotopes of different mass.

The idea that the atoms of an element are not all equally heavy was by no means absolutely new, but until then it had not been consistently followed up. Thus OSTWALD, in his *Schule der Chemie*, applies a damper to the overhasty conclusion of the pupil, namely that it was proved that all atoms of the same element were equally heavy, through the cautious counter statement of the tutor in which he causes the tutor to say in essence: "It is only proved that the atoms of an element cannot be separated by chemical means. Perhaps we shall one day possess a sieve fine enough to be able to sift them out from one another." Since, at the time when he wrote this, OSTWALD still inclined away from atomistics, he did not develop these ideas further (although, as this example shows, he was quite capable of thinking atomistically in a logical manner). In the year 1920, these ideas were taken up again, although in a different form, by F. W. ASTON, who set

himself the task of finding out in every case whether or not the elements consisted of isotopes, and further, of determining the masses of these isotopes with the greatest possible precision. The solution of both problems, which answers the question of the origin of the numerical values of the atomic weights and enables PROUT's hypothesis to be tested, was accomplished by ASTON with the help of his mass spectrograph. With this he first detected in neon the existence of three isotopes of masses 20, 21 and 22. In the course of time he had perfected his instrument to such a degree, that he was able to determine the relative proportions and masses of isotopes with a precision which at least equalled the precision of chemical atomic-weight determinations. Consequently a mutual control on the atomic weights determined by mass-spectrographical and chemical methods was possible. This will be referred to again later (p. 287 ff).

ASTON did not greatly concern himself with the search into the possibility of the *separation* of isotopes, which immediately arose on their successful detection, but left the matter to other investigators. In 1921, after a number of years' work, HARKINS³⁷ obtained a slight enrichment of the chlorine isotope ³⁷Cl by the diffusion of hydrogen chloride, and, more impressively, BRØNSTED and VON HEVESY³⁸ in 1922 separated mercury into a lighter and a heavier fraction which were plainly distinguishable in density as well as in atomic weight. Since then, improved and new kinds of separation procedures have been developed by which a large number of isotopes have already been obtained in a really pure state.

The present state of isotopic research will be outlined in a few paragraphs.

The mass spectrograph of ASTON³⁹ may serve for the *detection* of isotopes. This will not be described in detail here⁴⁰. For isotopes which are present in only very small quantities, the detection is conducted by optical means with the help of *molecular spectra*, in which the position of the lines is somewhat different, according to the masses of the atomic nuclei of the absorbing or emitting elements. Here avail can be made of the rotation spectrum in the far infra-red, of the rotation-vibration spectrum in the near infra-red or of the visible and ultra-violet spectra. From the magnitude of the displacement and the intensity of the lines relative to those of the most frequent isotope, the mass and abundance of the rare isotope can be calculated.

Examples of isotopes discovered in this manner include the oxygen isotopes ¹⁸O and ¹⁷O⁴¹. The absorption spectrum of oxygen contains lines which cannot be assigned to the completely symmetrical molecule ¹⁶O₂, but

³⁷ W. D. HARKINS and A. HAYES, *J. Am. Chem. Soc.*, 1921, **43**, 1803.

³⁸ J. N. BRØNSTED and G. VON HEVESY, *Phil. Mag.*, 1922, [vi], **43**, 31.

³⁹ F. W. ASTON, *Mass Spectra and Isotopes* (Arnold, London, 1933); *Proc. Roy. Soc.*, 1927, **A 115**, 487; J. MATTAUCH, *Z. tech. Physik*, 1937, **18**, 525.

⁴⁰ See, for example, A. EUCKEN, *Lehrbuch der chemischen Physik*, Vol. I, p. 30 ff (2nd Ed., 1938), where (p. 34) literature concerning mass spectrographs is quoted.

⁴¹ W. F. GIAUQUE and H. L. JOHNSTON, *Nature*, 1929, **123**, 831; *J. Am. Chem. Soc.*, 1929, **51**, 1436.

do correspond to the unsymmetrical molecules $^{16}\text{O}^{18}\text{O}$ and $^{16}\text{O}^{17}\text{O}$. The lines belonging to $^{16}\text{O}^{17}\text{O}$ are much the weaker. From the intensities, the relative proportions are $^{16}\text{O} = 99.8\%$, $^{18}\text{O} = 0.17\%$, $^{17}\text{O} = 0.03\%$.

The carbon isotope ^{13}C was discovered⁴² a little later than the oxygen isotopes by analysis of the so-called SWAN bands in the flame spectra of burning hydrocarbons, which are to be ascribed to the unstable C_2 molecule. This isotope is present to the extent of about 1% together with the isotope ^{12}C ⁴³.

The presence of the nitrogen isotope ^{15}N was concluded from the absorption bands of nitric oxide, among which, in addition to bands corresponding to $^{14}\text{N}^{16}\text{O}$, $^{14}\text{N}^{18}\text{O}$ and $^{14}\text{N}^{17}\text{O}$, those which could only be due to $^{15}\text{N}^{16}\text{O}$ occur⁴⁴. Only 0.3% is contained in ordinary nitrogen.

The hydrogen isotope $^2\text{H} = \text{deuterium D}$ was discovered by observations made on the line spectrum⁴⁵, which is ascribable to the atom, after its existence had been suspected because of a discrepancy between the atomic weights of hydrogen found by chemical and by mass-spectrographical means⁴⁶. The BALMER lines of deuterium are displaced by 1—2 Å with respect to those of hydrogen ^1H .

The separation of isotopes, either wholly or partly, is possible by the following methods:

Separation by fractional diffusion. — This rests upon the fact that the rate of diffusion of a particle depends upon its mass, rates of diffusion varying inversely as the square roots of the masses. At low pressures, the process approaches its object quicker than at atmospheric pressure. In this way, G. HERTZ⁴⁷ obtained the lighter neon isotope ^{20}Ne almost pure, whereas the heavy isotope ^{22}Ne , which is present in ordinary neon to the extent of only 9.73% — the isotope ^{21}Ne with 0.27% can be neglected here — was enriched to over 60%.

Separation by fractional evaporation. — (This is the so-called ideal-distillation method, during which no back-condensation of the evaporated particles takes place.) The lighter particles evaporate more quickly, that is, they leave the upper surface relatively more frequently than the heavier particles. Using this procedure, BRØNSTEDT and VON HEVESY⁴⁸ have enriched the lighter and heavier mercury isotopes.

Separation by fractional distillation is possible in principle, but proceeds,

⁴² A. S. KING and R. T. BIRGE, *Nature*, 1929, **124**, 127; R. T. BIRGE, *ibid.*, p. 182. ^{13}C is now obtained technically in America by the thermal diffusion of methane. In July 1945, one plant was producing $\frac{1}{2}$ gram monthly for 1000 dollars. Production is to be increased to 500 g per month, and the price reduced to 40 dollars per gram (*Chem. Eng. News*, 1946, **24**, 488).

⁴³ B. F. MURPHEY and A. O. NIER, *Phys. Rev.*, 1941, [ii], **59**, 771.

⁴⁴ S. M. NAUDÉ, *Phys. Rev.*, 1929, [ii], **34**, 1498; 1930, **35**, 130; **36**, 333.

⁴⁵ H. C. UREY, F. G. BRICKWEDDE and G. M. MURPHY, *Phys. Rev.*, 1932, [ii], **40**, 1.

⁴⁶ R. T. BIRGE and D. H. MENZEL, *Phys. Rev.*, 1931, [ii], **37**, 1669.

⁴⁷ G. HERTZ, *Z. Physik*, 1932, **79**, 108.

⁴⁸ See p. 282.

if at all, only very slowly. Thus, in the distillation of water for its separation into H_2O and D_2O , even though the boiling points are in this case much further apart than usual, the changes are imperceptibly small⁴⁹. Experiments to enrich the isotopes of chlorine by the distillation of carbon tetrachloride remained without success. With neon, on distillation in the neighbourhood of the triple point at -248° , a partition of ordinary neon, atomic weight 20.18, into two fractions of atomic weights 20.14 and 20.23 was achieved⁵⁰.

Thermal diffusion in a separation tube. — This process discovered by CLUSIUS and DICKEL⁵¹ appears at the present time to be the most advantageous and promising. With hydrogen chloride as the subject of the experiment, it was thereby possible for the first time to obtain a practical separation of the chlorine isotopes ^{37}Cl (99.4 % purity) and ^{35}Cl (99.6 % purity)⁵². Even when several isotopes are present, as in the case of krypton, for example, it attains its object.

Separation by the centrifuging of a gas. — The heavier particles are centrifuged outwards. The efficacy of the process is increased, according to the counter-current principle, by causing the gas stream in the outer part of the rotating gas to flow downwards, and at the axis upwards.

Separation in an electromagnetic field. — In this separation, the gas particles must first be ionized and the gaseous ions subjected to the action of an accelerating electric field. In the electromagnetic field, the heavier isotopes describe a curve of larger radius and emerge from the magnetic field at a point further from the centre of curvature than that at which the lighter isotopes leave.

The separation of the uranium isotope ^{235}U from ^{238}U , the isotope constituting the major portion of ordinary uranium, has been achieved by thermal diffusion, by diffusion through porous walls, by centrifuging and by electromagnetic separation. Uranium hexafluoride, subliming at 56° , was employed as the volatile uranium compound.

Separation by chemical reactions. — Isotopes differ in general so extraordinarily little as to chemical behaviour, that a separation by chemical means, which has also been tried⁵³, appears hopeless. The reason for this is to be sought in the fact that the structure of the electron envelope is decisive as far as chemical reactions are concerned, and this is in general only quite negligibly influenced by nuclei of somewhat different mass. This is

⁴⁹ G. N. LEWIS and R. E. CORNISH, *J. Am. Chem. Soc.*, 1933, **55**, 2616.

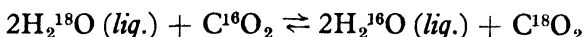
⁵⁰ W. H. KEESOM and H. VAN DIJK, *Proc. K. Acad. Wetensch. Amsterdam*, 1931, **34**, 42.

⁵¹ K. CLUSIUS and G. DICKEL, *Naturwissenschaften*, 1938, **26**, 546; *Z. physik. Chem.*, 1939, **B 44**, 397; 451.

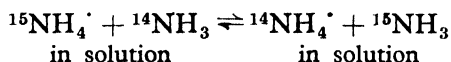
⁵² K. CLUSIUS and G. DICKEL, *Naturwissenschaften*, 1939, **27**, 487. Atomic weights: O. HÖNIGSCHMID and F. HIRSCHBOLD-WITTNER, *Z. anorg. Chem.*, 1939, **242**, 222.

⁵³ For example, B. KEETMAN's attempts to separate ionium from thorium, *Jahrb. der Radioaktivität und Elektronik*, 1909, **6**, 265; attempts to separate mesothorium I from radium by SODDY in 1911.

especially true for elements of higher atomic number, where the inner electron shells diminish the action of the nucleus on the valence electrons. Notable differences are certainly to be foreseen between hydrogen and deuterium, where the valence electron is subjected to the direct action of the nucleus. Of this there will be more to say later under heavy hydrogen. Feeble differences which can be utilized for a separation are nevertheless also extant in elements of the first period. Thus the equilibrium



lies very slightly in favour of C^{18}O_2 , which can be somewhat enriched by by volatilization⁵⁴, and the equilibrium



lies slightly in favour of ${}^{15}\text{NH}_3$. This can likewise be enriched by volatilization, in which gaseous ammonia evolved from ammonium sulphate solution and alkali under reduced pressure is allowed to flow in the opposite direction to a 30 % ammonium sulphate solution in a long fractionating column⁵⁵.

On electrolyzing water, the oxygen isotope ${}^{18}\text{O}$ becomes slightly enriched in the non-electrolyzed fraction. In this procedure, the enrichment of deuterium is much greater.

Heavy Hydrogen

The only isotopes which exhibit noteworthy differences in chemical behaviour as well as physical properties are the hydrogen isotopes of masses 1 and 2, of which the latter is usually called deuterium and also frequently represented by the symbol D instead of ${}^2\text{H}$. As already mentioned, the existence of deuterium was indicated by a discrepancy in the chemical and mass-spectroscopical atomic weights of hydrogen, from which it was already possible to calculate approximately the relative proportions of D and H. Proof of the presence of deuterium was very soon obtained by means of the spectrum. Of the various attempts to enrich it, practical success was realized only in the electrolysis of water⁵⁶, in which enrichment of deuterium oxide D_2O occurs in the residue. In this manner, from the water remaining undecomposed in industrial electrolysis equipment, pure D_2O could be obtained relatively easily by further electrolysis. Its density differs from that of ordinary water by about 10%.

⁵⁴ H. C. UREY and L. J. GREIFF, *J. Am. Chem. Soc.*, 1935, **57**, 321; L. A. WEBSTER, M. H. WAHL and H. C. UREY, *J. Chem. Phys.*, 1935, **3**, 129.

⁵⁵ H. C. UREY, M. FOX, J. R. HUFFMAN and H. G. THODE, *J. Am. Chem. Soc.*, 1937, **59**, 1407.

⁵⁶ E. W. WASHBURN and H. C. UREY, *Proc. Nat. Acad. Sci., U.S.*, 1932, **18**, 496.

	atomic weight	m.p.	b.p.	v.p. (mm) (temp. in °K)			mol. vol. at triple pt.	heat of vap ⁿ (cal/mol)	heat of fusion (cal/mol)
				13.92°	20.38°	23.5°			
H ₂	1.00813	-259.3°	-252.8°	54	760	1740	26.15	183	28
D ₂	2.01473		-249.7°	5	257	760	23.17	276	47

	m.p.	b.p.	d_4^{20}	d max. at	n_D^{20}	heat of vap ⁿ (cal/mol)	vis- cos- ity (20°)	surface tension (dyne/cm at 20°)	ionic mobility of H ⁺ , D ⁺ (mho)
H ₂ O	0.00°	100.0°	0.9982	4°	1.33300	9.70	10.09	72.75	(H ⁺) 315
D ₂ O	3.82°	101.42°	1.1059	11.6°	1.32844	9.96	12.6	67.8	(D ⁺) 214

The above two tables provide information concerning the differences in physical properties of H₂ and D₂ and of H₂O and D₂O. The compounds HD and HDO are also known, the latter in equilibrium with H₂O and D₂O (2HDO \rightleftharpoons H₂O + D₂O), but their properties are not reproduced here.

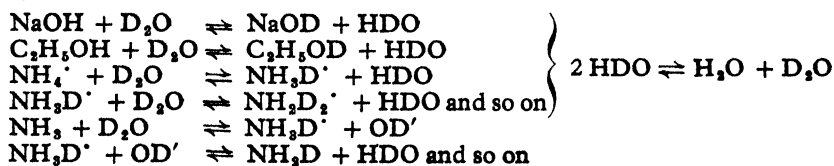
It is of theoretical significance that the magnetic moment of the proton with 2.79 nuclear magnetons is appreciably greater than that of the deuteron with 0.86 nuclear magnetons⁵⁷ (cf. p. 296 ff).

With regard to the chemical reactions of the two isotopes and their compounds, the following will be mentioned:

In accordance with the firm binding of the atoms in the molecules, deuterium D₂ first reacts with hydrogen H₂ around 700°, whereupon an equilibrium between D₂, H₂ and HD is set up⁵⁸. With known hydrogenation catalysts, equilibrium is already attained at the temperature of liquid air.

The rate of reaction of hydrogen and deuterium with the same reaction partners can under certain circumstances be really markedly different, as in the cases of chlorine and bromine. Here deuterium reacts more slowly. For the reaction with bromine, the activation energies 17.7 kcal for H₂ and 19.9 kcal for D₂ have been calculated from the temperature coefficients.

Substances which form hydrogen ions, even to only a very minute extent, exchange ionizable hydrogen and ionizable deuterium in an immeasurably short time. Such an exchange occurs, for example, in the hydroxyl compounds, as also in ammonia and the amines:



⁵⁷ S. MILLMAN and P. KUSCH, *Phys. Rev.*, 1941, [ii], 60, 91 (2.7896 \pm 0.0008 for H, 0.8565 \pm 0.0004 for D); J. M. B. KELLOGG, I. I. RABI, N. F. RAMSEY (Jr) and J. R. ZACHARIAS, *ibid.*, 1939, [ii], 55, 595; 56, 728 (2.785 for H, 0.855 for D).

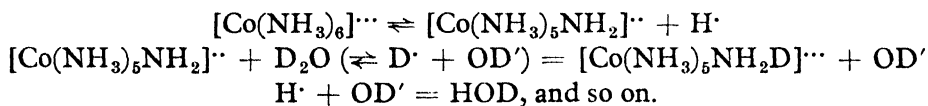
⁵⁸ A. J. GOULD, W. BLEAKNEY and H. S. TAYLOR, *J. Chem. Phys.*, 1934, 2, 362.

Non-ionizable hydrogen is not exchanged, *e.g.*, the hydrogen of the alkyl groups in the alcohols or amines. An exchange of the alkyl groups takes place only if a tautomerizable compound reacts with D_2O under conditions for which tautomerism occurs. Acetone $(CH_3)_2C=O$ thus dissolves in D_2O without change and can be regained unchanged from the solution by distillation. In the presence of alkali, however, which gives rise to the formation, even if only in traces, of the tautomeric enol form $CH_3-C=CH_2$



containing a hydroxyl group with exchangeable hydrogen, an exchange does occur⁵⁹.

The hydrogen in ammonia is immediately exchanged via the NH_3D^+ ion, according to the equations given above. In contrast, exchange in the stable ammine-complexes of the type of the hexammine-cobaltic ion $[Co(NH_3)_6]^{++}$ requires a measurable time dependent on the hydrogen-ion concentration of the solution, the velocity being inversely proportional to the latter. It is consequently to be assumed that a very slight ionization of the complexly bound NH_3 with resultant exchange occurs, this being retarded by suppression of ionization effected by hydrogen ions:



Water and heavy water are not equally good solvents. Thus, the solubilities of sodium chloride and barium chloride, for example, are less in heavy than in ordinary water. At 25° , 100 g H_2O dissolve 35.9 g NaCl and 35.7 g $BaCl_2$; 100 g D_2O , on the other hand, dissolve only 30.5 g NaCl and 28.9 g $BaCl_2$. It is simultaneously seen from these two examples that, on the substitution of H_2O by D_2O , the solubilities of various salts are not altered in the same ratio.

8. PROUT'S Hypothesis in the Light of Modern Research. Concerning the Structure of the Atomic Nucleus

(i) Packing Fraction

Mass-spectroscopy enables masses and relative proportions of the isotopes to be determined, and thereby provides the answer to the question of how the atomic weight of an element comes about. If it is not a pure element which is under observation, this atomic weight is a *mean* atomic weight, which is without particular significance for atomic research and not a fundamental quantity which must be measured with great precision for

⁵⁹ The enol form need not necessarily be formed. Detailed discussion: W. HÜCKEL, *Theoretische Grundlagen der organischen Chemie* I, pp. 390—391 (6th Ed., 1949).

its own sake, rather like the quantum of action, the LOSCHMIDT number, or the $\frac{e}{m}$ ratio for the electron. Rather, the classical atomic weight is, as it were, resolved into two constituents, the masses of the individual isotopes and their relative proportions. Because of this, two lines of research result. The first question concerns the precise dimensions of the isotopic masses, and how they are interrelated. The other line of investigation is the sequel of the striking ascertainment which was made on drawing up the classical atomic weights, namely, how it should come about that about 20 elements are pure elements, and for about a further 10 elements the proportion of one isotope so preponderates that the atomic weight is practically equal to that of the pure element — *e.g.*, for H, He, Be, C, N, O, Si and S — whereas for other elements numerous isotopes occur side by side in not very different quantities, as for molybdenum, tin and mercury. This question leads ultimately to the problem of probability of formation of the various atomic nuclei and to the problem of their stability. These two questions are in turn connected with the question of the abundance of the elements.

In order to obtain an answer to all these far-reaching questions, one must first have proceeded in the former of the two above-mentioned lines of investigation, be acquainted with the exact atomic weights of the isotopes, and know how these numbers are connected with the structure of the atomic nucleus.

With his hypothesis, PROUT had already expressed suspicion that the nucleus of the atom of any particular element is not something that has existed from the beginning, but is built up of smaller structural units. Today, one is led directly to this hypothesis by reason of reliable observational material concerning the atomic weights of pure types of atoms. At first sight they appear as integral multiples of the atomic weight of hydrogen. Trivial deviations from integral numbers certainly occur, but they are contained within much narrower limits than in the case of the classical atomic weights for the mixed elements and are essentially regular. Throughout, the mass of an atomic nucleus is somewhat smaller than is calculated from the sum of the masses of a whole number of hydrogen atoms. Thus, for example, the mass of deuterium = $2H - 0.00153$, and of helium, where the deviation is especially large, $4H - 0.02863$. The difference ΔM with respect to the calculated integral value is named the *mass defect*. Frequently, one reckons instead with the relative mass defect $\frac{\Delta M}{M}$ referred to the unit of mass.

But since atomic weights are not referred to hydrogen as the unit, but to O = 16.000, it is usually not the relative mass defect which is used for purposes of comparison, but the deviation from whole numbers referred to the usual unit of the atomic-weight scale, for which it is divided by the

nearest atomic weight. This quantity is designated after ASTON as the *packing fraction*. Its numerical values do not give a direct picture of the true mass defect in the sense of PROUT's hypothesis, and have as such no physical significance. This can be directly concluded from the fact that for hydrogen which has the atomic weight 1.008, a *positive* packing fraction of $\frac{+0.008}{1} = 8 \times 10^{-3}$ is calculated in the above manner. It is thus convenient

in calculating packing fractions simply to employ the numerical values of the ordinary atomic-weight tables extended to the individual isotopes, so that one makes use of the numbers directly obtainable from them. In this manner of reckoning, the packing fraction for oxygen is arbitrarily put equal to zero. The packing fractions of the pure elements arsenic ^{75}As and gold ^{197}Au may be calculated as examples:

$$\text{mass of } ^{75}\text{As} = 74.91, \quad \Delta = -0.09, \quad \frac{\Delta}{M} = \frac{-0.09}{75} = -1.2 \times 10^{-3};$$

$$\text{mass of } ^{197}\text{Au} = 197.2, \quad \Delta = +0.20, \quad \frac{\Delta}{M} = \frac{+0.20}{197} = +10^{-3}.$$

If the dependence of the packing fraction on atomic mass is plotted, it is possible to draw a curve between the points from which the individual values are in general not far removed (Fig. 31a, 31b). Only the values for

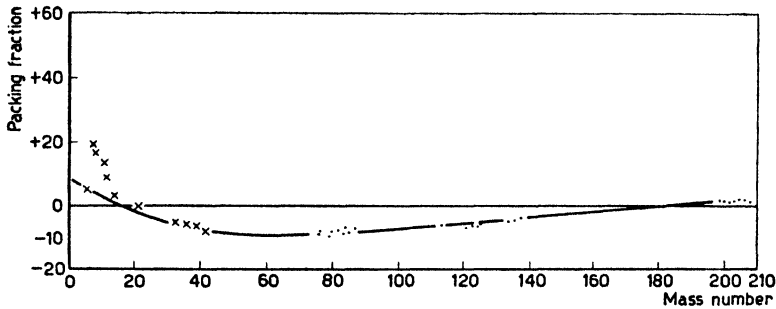


Fig. 31a. Packing fractions from He to Bi multiplied by 10^4 . The value for H lies off the figure at +80 close to the ordinate.

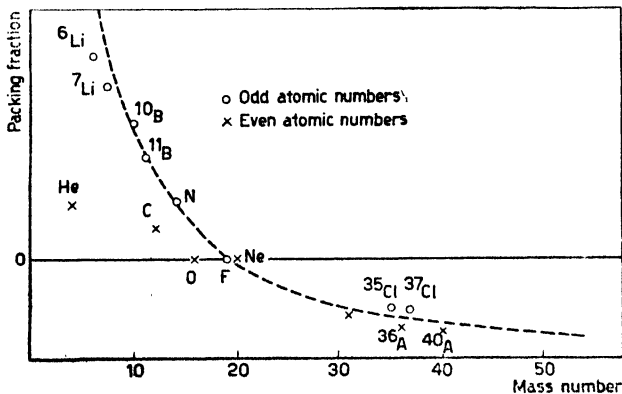


Fig. 31b. Packing fractions from He to A

helium, carbon and oxygen lie appreciably below the curve, which cuts the abscissa firstly at ^{19}F , this, like oxygen, having a packing fraction of zero. The curve, which first falls steeply from hydrogen to fluorine, soon becomes flat and reaches a minimum lying at about -1×10^{-3} in the region of mass numbers 50 to 75: it then slowly rises again. For atomic masses of about 200 onwards, the packing fraction becomes weakly positive, that is, the relative mass defect is here somewhat smaller than for oxygen.

The *packing fraction* is a hypothesis-free dimension standing upon the empirical foundation of ordinary atomic weights. The relative *mass defect*, referred to the mass of the hydrogen atom as unit, has, by way of contrast, PROUT's hypothesis as theoretical background. Commencing with the very close approximation of atomic weights of the individual species of atoms to whole numbers, it presupposes that the masses of the atomic nuclei are built up from hydrogen nuclei. Attractive as this hypothesis is on account of the proximity to whole numbers, it nevertheless needs to be supported by experiments from which it follows that protons take part in the building up of nuclei. With the supposition that this is the case, the mass defect can be theoretically understood.

Before examining this, the significance of the choice of oxygen with 16.000 as the basis of atomic weights will be discussed for the numerical results of the individual atomic weights relative to the earlier, frequently employed and, in part, stoutly defended basis of hydrogen with 1.0000. In conjunction therewith, the fact of the mass defect and the trend of the packing-fraction curve will also be considered. In consequence of the mass defect, as the initial very steep fall in the packing-fraction curve from hydrogen indicates, the masses of all the atomic nuclei are appreciably smaller than corresponds to integral multiples of hydrogen. The height of the packing fraction assigned to hydrogen, namely $+8 \times 10^{-3}$, is not even approached by any other atom. The nearest is lithium with $+2 \times 10^{-3}$. Consequently atomic weights of pure atomic species referred to $\text{H} = 1.0000$ must have values which, without exception, fall appreciably below whole numbers. On the other hand, if $\text{O} = 16.000$ is chosen as the basis, the atomic weights are thereby referred to the weight of an atom, the oxygen atom, in which the mass defect is already present, and not very different from the relative mass defects of the remaining elements. The result is that the atomic weights referred to $\text{O} = 16.000$ lie much nearer to whole numbers than those referred to $\text{H} = 1.0000$.

Strictly speaking, on account of the fact that oxygen consists of a number of isotopes, it still makes a difference whether atomic weights are referred to ordinary oxygen with $\text{O} = 16.000$, which is the *chemical* basis of atomic weights, or whether the oxygen isotope 16 is taken as a reference point at 16.000, this being the *physical* basis of atomic weights. The choice between the chemical and physical bases of atomic weights is by all means without importance for the degree of approximation of the atomic weights to whole numbers, for the physical atomic weight of ordinary oxygen is 16.004 35

$\pm 0.000\ 086$ and the factor for converting from the chemical to the physical basis $1.000\ 272 \pm 0.000\ 005$, which makes a much smaller contribution than the differences in the packing fractions.

The deviations of the atomic weights of the individual atomic species from whole numbers comprised in the packing fractions do not conflict with PROUT's hypothesis that atomic nuclei are built up of protons. The mass defect which receives expression in these deviations does not imply a correction to this hypothesis, which, in its fundamentals, is not affected. If the atomic nuclei are constructed of protons, then a mass defect *is to be expected*, in the event that unusually large quantities of energy are liberated on their formation. The law of conservation of mass for chemical processes no longer holds within the limits of precision obtainable in the measurements, for the masses building up the nucleus do not add up simply, but appear to be *decreased* by a certain amount, the magnitude of which is related to the energy of formation. This, as we now know, has an order of 10^5 kcal, that is 10^3 to 10^4 times as much as for ordinary chemical reactions. This follows from the energy of the radiation which is emitted on nuclear transformations. The decrease in mass $-\Delta M$ of the combining masses, as can be theoretically established, is related to the evolved energy ΔE by the relation

$$-\Delta M = \frac{\Delta E}{c^2},$$

where c is the velocity of light. It is precisely from the balance of energy and mass in nuclear processes that the confirmation of this law has been possible ⁶⁰.

(ii) Nuclear Transmutations and Nuclear Particles

From nuclear transmutations something is also learnt about the component particles which form the nucleus. Formerly, when fewer nuclear reactions were known than are today, it was believed that the nuclei consisted of protons and electrons, their masses, corresponding to PROUT's hypothesis, thus being given by the number of protons contained in them. In this, small corrections are still to be applied to the sums of the masses of the protons, corrections which take into consideration the masses of the electrons included in the nuclei and the mass defect. As may at once be anticipated here, it is now known that for various reasons this assumption cannot be correct, and that PROUT's hypothesis does not quite hit the truth. Atomic nuclei are in fact formed from two structural particles which together constitute the mass, namely protons and neutrons. The neutron is an uncharged particle of almost exactly the same mass as the proton, so that it makes very little

⁶⁰ Particularly comprehensive confirmations are provided by the investigations of W. BRAUNBEK, *Z. Physik*, 1937, **107**, 1. See further the reviews of S. FLÜGGE and A. KREBS, *Physik. Z.*, 1937, **38**, 13; M. S. LIVINGSTON and H. A. BETHE, *Rev. Modern Phys.*, 1937, **9**, 245.

difference for the mass of a nucleus whether it is composed only of protons, or of protons plus neutrons. Experiments which have led to the modern conception of the structure of the nucleus rest on various nuclear transmutations, as will be portrayed in the following. In this it will also become understandable why it was formerly believed that nuclei were constructed of protons and electrons.

By way of nuclear processes, artificial nuclear transformations⁶¹ as well as radioactive decay are known today. The former can be effected by the bombardment of nuclei with α -particles = ${}^4\text{He}^{++}$, protons = ${}^1\text{H}^+$, deuterons = ${}^2\text{H}^+$ or D^+ , neutrons = 1n , and by very hard γ -radiation. The same particles can also be set free as "nuclear fragments" in nuclear reactions, in which hard γ -radiation can also occur. The nuclear reactions can be characterized by a terse and precise symbology according to the particles which effect them and the fragments shot off from the nuclei. In this, the particles and γ -radiation are respectively abbreviated to α , p , d , n and γ . An $\alpha;p$ process is a nuclear reaction in which an α -particle collides with the nucleus and thereby sets free a proton, whereas in a $p;\alpha,\gamma$ process, the nucleus is bombarded with a proton, and releases an α -particle with the emission of γ -radiation, and so on.

The first nuclear transformations to become known were the decay processes of the nuclei of radioactive elements, which it has not so far been possible to influence in any artificial manner. In these processes, either α -rays or β -rays are expelled as material particles from the decaying nucleus, whereupon γ -rays, which possess a spectrum, are also emitted. In this, therefore, the proton did not make its appearance as a unit of nuclear structure. The proton was first observed in the original *artificial* nuclear transformation which RUTHERFORD realized in 1919 by the bombardment of nitrogen with α -particles, in which a proton flies out of the nucleus. It can be easily distinguished from the α -particles by its great range. At first, RUTHERFORD believed that the nitrogen nucleus had been shattered by the bombardment. It later became apparent that the missile remained adhered to the nitrogen nucleus with the formation of the oxygen isotope of mass 17, while it ejected a proton. Thus the synthesis of a nucleus occurs which is represented in equation form by the $\alpha;p$ transformation ${}^{14}_7\text{N} + {}^4_2\text{He} = {}^{17}_8\text{O} + {}^1_1\text{H}$, or more completely ${}^{14}_7\text{N} + {}^4_2\text{He} = {}^{17}_8\text{O} + {}^1_1\text{H}$. In equations of this type, it is frequently customary to give in addition to the mass of the nucleus at the upper left-hand corner of the symbol also the nuclear charge (= atomic number) at the lower left-hand corner, in order to intimate that in such nuclear processes the law of conservation of charge holds true as well as the law of conservation of the sums of the rounded masses. Thus, in the above example,

⁶¹ Artificial nuclear transformations, γ -rays, neutrons, positrons: R. FLEISCHMANN and W. BOTHE, *Ergebn. exakt. Naturw.*, 1934, **13**, 1. Easily readable and very clear presentation of the knowledge obtained up to 1935: P. DEBYE, *Z. angew. Chem.*, 1935, **48**, 381.

- (a) $7 + 2 = 8 + 1 = 9$ for the charge, and
 (b) $14 + 4 = 17 + 1 = 18$ for the rounded masses.

Since, consistently, in numerous artificial nuclear processes and in natural radioactive disintegrations only α -particles, protons and electrons were obtained and it remained at that, the view was held for over ten years that atomic nuclei were constructed of these. The α -particle did not, as a structural unit, thereby fall outside the framework of PROUT'S hypothesis thus extended, inasmuch as it could be thought of as built up of four protons and two electrons which must be particularly firmly bound together — to which fact the large mass defect for helium pointed — so that they remained united in the nuclear processes.

However, the position was changed at a single stroke when in the year 1932 a new material particle, the *neutron*, was discovered. It had escaped observation for so long because it is uncharged and consequently leaves no condensation track behind it in the WILSON cloud chamber, as do α -particles protons and electrons, all of which produce ions on their passage through a gas. One became aware of the presence of the neutron when the energy of the γ -radiation produced on bombarding beryllium or lithium with α -particles proved to be independent of the energy of the incident α -particles⁶².

Since there is a contradiction of the law of conservation of energy when collision processes of different energies cause nothing but a radiation of constant energy, another process besides the emission of γ -rays must occur. In another similar experiment, the bombardment of boron, such a process was the emission of a proton along with the γ -radiation, but in the cases of beryllium and lithium there were no traces of protons to be detected in the WILSON cloud chamber. However, it became apparent, on closely examining the gas which, in addition to water vapour, filled the chamber, that free atoms had been liberated, hydrogen atoms from hydrogen molecules and nitrogen atoms from nitrogen molecules. Further, it became apparent that the emitted radiation could also knock out protons from paraffin wax, which γ -radiation is not able to do⁶³. The explanation for this originally puzzling observation was supplied by CHADWICK⁶⁴ by the assumption of an uncharged particle, which he named the *neutron*. It was supposed to arise in addition to γ -radiation on the bombardment of beryllium. When he succeeded in calculating the approximate mass of the neutron from the observed recoil energies of the accelerated atoms of the gas in the WILSON cloud chamber and in this way bringing the energy balance of the nuclear transformation into order, he was able to regard the exact proof for the existence of the *neutron* as adduced. According to this, the mass of the neutron was about equal to the mass of the proton.

⁶² H. BECKER and W. BOTHE, *Naturwissenschaften*, 1932, **20**, 349; *Z. Physik*, 1932, **76**, 421.

⁶³ I. CURIE and F. JOLIOT, *Compt. rend.*, 1932, **194**, 876.

⁶⁴ J. CHADWICK, *Proc. Roy. Soc.*, 1932, **A 136**, 692.

Later, the neutron was obtained from beryllium, likewise by the use of very hard γ -radiation (as produced by the very short-lived thorium C'', a β -emitter of half-life 3.1 min). It was further observed that the same radiation effected a splitting of deuterium into a proton and a neutron⁶⁵. The latter observation has become important for the understanding of the structure of the atomic nucleus. In addition, it enabled a very precise determination of the mass of the neutron to be made. This yielded that the mass of the neutron is very similar, but not exactly equal to that of the hydrogen atom:

$$\begin{aligned} {}^1_1\text{H} &= 1.008\,128\,4 \pm 0.000\,002\,7, \\ {}^1_1\text{H}^+ \text{ (proton)} &= 1.007\,579\,8 \pm 0.000\,002\,8, \\ {}^1_0\text{n} &= 1.008\,937 \pm 0.000\,005\,^{66}. \end{aligned}$$

The neutron is given the symbol ${}^1_0\text{n}$ or, more completely ${}^1_0\text{n}$, since it has a mass of unity but a zero nuclear charge. Because the latter is identical with the atomic number, the neutron stands in the Periodic System before hydrogen as the element with atomic number 0.

It has been possible to effect numerous new kinds of nuclear transformations with neutrons, which are especially suited to this purpose since they are not electrostatically repelled on approaching the nuclei of the bombarded atoms. Because of this, bombardment with slow neutrons is also effective, often more effective than with fast neutrons. New kinds of nuclear fragments do not of course occur thereby. By bombardment with neutrons, in $n;\alpha$, $n;p$, $n;2n$ and $n;\gamma$ processes an α -particle, proton (the deuteron has not so far been observed) or a second neutron is liberated from the nucleus; alternatively, γ -radiation is produced. It may also happen that the neutron simply remains in the nucleus in an $n;$ - process. The shattering of very heavy atomic nuclei by neutron bombardment, which leads in the case of the uranium isotope 235, for example, to strongly β -emitting isotopes of barium and krypton, as well as other fission fragments⁶⁷ — among which some thirty different elements from selenium upwards and about a hundred atomic species have been observed — does not belong here and comprises a whole subject on its own. The synthesis of the trans-uranic element 93 (neptunium) by the action of neutrons on the uranium isotope 238, and the further transformation of element 93 into element 94 (plutonium), an isotope of which is the active principle in the atomic bomb, will be discussed later. But, on account of the great significance of these fission processes undergone by atomic nuclei, this much must be mentioned here, namely that nuclear fission of this type has so far been reported only for the following atomic species: ${}^{233}\text{U}$ (from thorium), ${}^{235}\text{U}$ (but *not* ${}^{238}\text{U}$), protactinium ${}^{231}\text{Pa}$ and plutonium ${}^{239}\text{Pu}$.

⁶⁵ J. CHADWICK and M. GOLDBABER, *Proc. Roy. Soc.*, 1935, **A** 151, 479.

⁶⁶ K. KIMURA finds 1.00895: *Mem. Coll. Sci. Kyoto Imp. Univ.*, 1939, **A** 22, 237.

⁶⁷ O. HAHN and F. STRASSMANN, *Naturwissenschaften*, 1938, **26**, 755; 1939, **27**, 11; 163; 1940, **28**, 54. It was formerly believed that on bombarding uranium with neutrons, isotopic uranium was formed which subsequently changed by β emissions into elements of higher atomic number, the so-called trans-uranic elements.

The discovery of the *positron*, the positive counterpart of the electron, by ANDERSON⁶⁸ in the year 1933 has remained without significance with respect to the theory of nuclear structure, although, as was later observed, positrons also appear with the decay of artificially produced radioactive species of atoms (but do not accompany natural radioactivity). Thus, for example, the radioactive nitrogen isotope ^{13}N (see later) decays into ^{13}C plus a positron. Although it is here ejected from the nucleus, it is not included in the structural units of the nucleus. The reasons for this are the same as in the case of the electron, which will now receive discussion.

The particles which are given off by nuclei can be divided according to their mass and manner of formation into two groups. Under the collective name *nuclear fragments*, the heavy particles — α -particles, protons, occasionally deuterons and neutrons — are produced directly by the elementary act of a nuclear transformation which requires no measurable time. Electrons and positrons, particles lighter by some three powers of ten, are formed only in the course of radioactive disintegrations which can be followed in time, electrons from natural as well as artificial β -emitters, and positrons only from certain species of radioactive atoms. The emission of electrons or positrons from the nuclei has nothing to do with the elementary act which leads to the formation of artificial radioactive species, for the radioactive decay is completely independent of the manner of formation. Two examples of this will be given.

The half-life period of the radioactive nitrogen isotope ^{13}N (\rightarrow ^{13}C + positron) is 11 minutes, irrespective of which of the following ways it is obtained:

- (i) by the $\alpha;p$ process $^{10}\text{B} + ^4\text{He} = ^{13}\text{N} + ^1\text{H}$,
- (ii) by the $d;n$ process $^{12}\text{C} + ^2\text{H} = ^{13}\text{N} + ^1n$,
- (iii) by the $n;2n$ process $^{14}\text{N} + ^1n = ^{13}\text{N} + 2^1n$.

The radioactive aluminium isotope ^{28}Al with half-life period 2.1 minutes can be formed in as many as five different ways :

- (i) the $n;$ - process $^{27}\text{Al} + ^1n \rightarrow ^{28}\text{Al}$,
- (ii) the $n;\alpha$,, $^{31}\text{P} + ^1n \rightarrow ^{28}\text{Al} + ^4\text{He}$,
- (iii) the $n;p$,, $^{28}\text{Si} + ^1n \rightarrow ^{28}\text{Al} + ^1\text{H}$,
- (iv) the $\alpha;p$,, $^{26}\text{Mg} + ^4\text{He} \rightarrow ^{28}\text{Al} + ^1\text{H}$,
- (v) the $d;p$,, $^{27}\text{Al} + ^2\text{H} \rightarrow ^{28}\text{Al} + ^1\text{H}$.

The fundamental difference in the manner of formation of the heavy and light particles suggests the assumption that the time-requiring production of light particles succeeds by a secondary process in which the particles from which the nucleus is genuinely constructed, and which are united in an unstable and consequently radioactive nucleus, undergo spontaneous changes. It is not possible to perceive in these considerations a conclusive proof that no light particles are "contained", that is to say, to some extent typified in the nucleus.

⁶⁸ C. D. ANDERSON, *Phys. Rev.*, 1933, [ii], 43, 491; 44, 406. ANDERSON discovered the positron during his studies of penetrating cosmic radiation.

(iii) Nuclear Spin

Such a proof, which excludes the existence of independent electrons in the nucleus, is however supplied from observations concerning *nuclear spin*. One is led to assume the existence of such by the structure of spectral lines which have been resolved as far as possible by means of the most delicate of interference spectroscopes. In this manner, it has become apparent that with most elements a so-called *hyperfine structure* is present. This is incomprehensible as long as the nucleus of the atom is regarded simply as a point which is fully described by its mass and its co-ordinates in space. For an explanation it is essential that a *spin* be ascribed to the nucleus in the manner necessary for the electron. The nucleus thus possesses an angular momentum brought about by a gyroscopic motion, which can result in a magnetic moment. This magnetic moment of the nucleus, is, according to its mass, more than three powers of ten smaller than the moment derived from the spin of the electron, which is already an argument against the assumption of electrons in the nucleus. The hyperfine structure can be quantitatively explained by the magnetic action of the nucleus rotating about an axis when the angular momentum of the nucleus is characterized by a quantum number I and vectorially added to the angular momentum of the electron envelope denoted by the quantum number J . In this, there are, according to the quantum theory, various configurational possibilities of gyration which correspond to different interaction energies, and thereby lead to a splitting of the spectral lines. The theory cannot be given in detail here.

The nuclear spin now stands in close relation to the structure of the nucleus. Whatever form this has, it follows that the nuclear spin depends on the *mass number* of the nucleus, and not on its charge number. The following rule is valid without exception: Atoms with odd mass numbers have nuclear spins with half-integral quantum numbers, atoms with even mass numbers either have a nuclear spin with the quantum number 1 or none at all. The two hydrogen isotopes accordingly possess different nuclear spins with ${}^1\text{H} = \frac{1}{2}$ and ${}^2\text{H} = 1$, as has been ascertained in this case by direct determination of the magnetic moment of the nucleus by the atomic-beam method⁶⁹ (cf. p. 262). For the remaining elements, the nuclear spins, as far as they are known, have been derived from the hyperfine structures.

A construction of the nucleus from protons and electrons cannot be brought into harmony with this rule, but a construction from protons and neutrons *can* if a spin moment characterized by the quantum number $\frac{1}{2}$ is ascribed to the latter, as to the protons. The two hypotheses concerning

⁶⁹ I. ESTERMANN and O. STERN, *Z. Physik*, 1933, **85**, 17; **86**, 132 (nuclear moment of H 2.46 nuclear magnetons); *Nature*, 1934, **133**, 911 (nuclear moment of D 0.7 nuclear magnetons). More recent values are 2.79 and 0.86 respectively (see p. 286, footnote 57). For the calculation of one nuclear magneton as unit, the same formula holds as for the calculation of the BOHR magneton, but with a mass 1840 times as large.

the construction of the nucleus lead namely to different conclusions with respect to the nuclear spin. With a nucleus built up from protons and electrons it would have to be dependent upon the atomic number, with a nucleus built up from protons and neutrons upon the mass number. This follows from the following considerations.

The number of nuclear particles a nucleus of mass number M and charge number Z contains, in the event that it is constructed of protons and electrons, is $N_p = M$ protons plus $N_e = M - Z$ electrons. The mass arises solely from the protons. If, on the other hand, the nucleus consists of protons and neutrons, not its entire mass but its entire charge depends upon the protons. In this case the number of particles is $N_p = Z$ protons plus $N_n = M - Z$ neutrons.

If the nucleus is built up of protons and electrons, both of which have the spin quantum number $\frac{1}{2}$, then the total spin depends on the sum of the number of protons, N_p , and electrons, N_e , in the nucleus, which is $2M - Z$. The nuclear spin should thus be integral if this sum $2M - Z$ is an even number, which it is if Z is even. The nuclear spin must here appear as a function of Z and be integral for elements with atomic number even, and half-integral for those with atomic number odd.

On the other hand, if the nucleus is constructed of protons and neutrons, then the nuclear spin is given by the sum of the spins of the protons and neutrons, which is $Z + M - Z = M$. Thus the nuclear spin becomes a function of the mass number M . For mass numbers which are odd it becomes half-integral.

The following examples show that the nuclear spin depends in this way on the mass number. The nuclear spin of deuterium, whose nucleus consists of a proton and a neutron, is $\frac{1}{2} + \frac{1}{2} = 1$. If it consisted of two protons and an electron, it would be either $\frac{1}{2} + \frac{1}{2} + \frac{1}{2} = \frac{3}{2}$ or $\frac{1}{2} + \frac{1}{2} - \frac{1}{2} = \frac{1}{2}$. Moreover, the nuclear spin of the nitrogen atom with the even mass number $M = 14$ and the odd charge number $Z = 7$ is equal to 1. The oxygen atom with $M = 16$ and $Z = 8$ has no nuclear spin, which would be equally possible with a nucleus of protons and neutrons as with one of protons and electrons.

Even after it is known that protons and neutrons build up the nuclei, important questions still remain. First comes the question which concerns the properties of the neutron. In order that the nuclear spin comes out correctly, it has been assigned a spin of $\frac{1}{2}$. Its magnetic moment has been found to be 1.935 ± 0.02 nuclear magnetons⁷⁰, close to the difference between that of the proton and that of the deuteron. Also, it must first and foremost be explained theoretically how it is that the rotation of a completely uncharged particle produces a magnetic moment. If one clings to the point that a magnetic field arises through the motion of electric charge, one is obliged to assume a definite electric structure for the neutron. It is conceivable that the neutron is capable of breaking up into a proton and

⁷⁰ L. W. ALVAREZ and F. BLOCH, *Phys. Rev.*, 1940, [ii], 57, 111.

an electron according to a kind of radioactive β -decay process⁷¹. This would also answer the question why there are two elementary particles of almost exactly the same mass.

The question of a possible disintegration of the neutron is linked with the question of β -decay, or still more generally with the question of how it is possible in the spontaneous disintegration of unstable nuclei for electrons and positrons to be ejected without having previous existence in such nuclei. And, also, when it is known that nuclei are constructed of protons and neutrons, it is still not clear what are the forces which hold the two particles together, nor how strong they are. A study of this question leads to the problem of stability of the nuclei. Its solution, towards which nuclear physics strives, must ultimately lead to the explanation of the rules, which have so far been found empirically, concerning the occurrence and abundance of the isotopes. Such rules, which today are still largely not understood, include the following:

Generally speaking, elements with even atomic numbers are more abundant than their neighbours in the Periodic System with odd atomic numbers (HARKIN's Rule). The number of isotopes is greater for elements with even atomic numbers than for elements with odd atomic numbers.

Isotopes of elements with odd atomic numbers have in general odd mass numbers. Of these, at most only two stable isotopes occur, which differ by two units in the mass number, that is, by two neutrons in the nucleus. A stable nucleus possesses a mass number at least double its atomic number. It thus contains as many or more neutrons than protons. The only exceptions to this are the proton and neutron themselves.

Of two isobaric atoms differing in nuclear charge by 1, one is unstable (MATTAUCH's Rule)⁷².

9. Trans-Uranic Elements

As already mentioned, in addition to the fission which the ^{235}U nucleus undergoes on bombardment with slow neutrons, the action of neutrons on the uranium nucleus can in the case of the nucleus of the ^{238}U isotope — which does not break up — also result in a nuclear synthesis. In this synthesis, one arrives by radioactive changes at elements possessing higher atomic numbers than that of uranium. Of these, elements with the atomic numbers 93 to 98, in some cases in a number of isotopic forms, have become known during the years 1940 to 1950. The most important facts concerning the production and properties of these elements, of which element 93, neptunium, and element 94, plutonium, have been the more closely studied, will be briefly given in the following.

⁷¹ E. FERMI, *Z. Physik*, 1934, **88**, 161.

⁷² J. MATTAUCH, *Z. Physik*, 1934, **91**, 361.

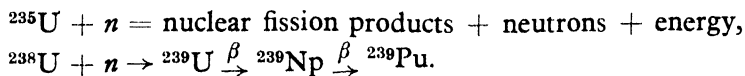
Production of element 93, neptunium. — (i) The isotope ^{239}Np is a β -emitter of half-life period $\tau = 2.3$ days. It is formed via ^{239}U , a β -emitter with $\tau = 23$ minutes, from ^{238}U by bombardment with neutrons from the cyclotron of E. O. LAWRENCE. It was discovered in May 1940 by E. McMILLAN and P. H. ABELSON. The processes can be briefly expressed: $^{238}\text{U} + n \rightarrow ^{239}\text{U} \xrightarrow{\beta} ^{239}\text{Np}$.

(ii) The isotope ^{237}Np is an α -emitter with the half-life period $\tau = 2.25 \times 10^6$ years. It is formed in the following way. ^{238}U gives, in an $n;2n$ transformation with fast neutrons, ^{237}U , a β -emitter with $\tau = 7$ days (this succeeding exactly like the formation of ^{13}N from ^{14}N cited on p. 295). ^{237}Np is produced from ^{237}U by β emission. This method was discovered by A. C. WAHL and G. T. SEABORG early in 1942. On account of its long half-life period, it is more suitable for investigating the chemical properties than the isotope of mass 239. From it, B. MAGNUSSON and T. J. LA CHAPELLE prepared the first chemically pure compound of neptunium to be obtained in weighable quantities.

(iii) The isotope ^{238}Np is a β -emitter with $\tau = 2.0$ days. It is formed in the bombardment of ^{238}U with deuterons from the cyclotron by a $d;2n$ transformation (a nucleus with charge 1 and mass 2 entering the uranium nucleus which loses two neutrons with the same total mass).

Production of element 94, plutonium. — (i) The isotope ^{238}Pu , an α -emitter of half-life 50 years, is the element which arises by β emission from the last-named isotope of neptunium, ^{238}Np . Its formation was observed by G. T. SEABORG, E. McMILLAN, A. C. WAHL and J. W. KENNEDY at the end of 1940.

(ii) The isotope ^{239}Pu , an α -emitter with $\tau = 24 \times 10^3$ years, arises through β emission from the rapidly decaying ^{239}Np . Its formation can be effected in larger amounts if ^{238}U is transformed not by direct neutron bombardment, but by making use of the neutrons liberated by the very rapid fission of the uranium isotope 235:



The neutrons originating from ^{235}U must be slowed down, which is accomplished by embedding rods consisting of uranium in pure graphite, which is not a neutron absorber. The process is allowed to proceed in an arrangement known as a "pile", which must be surrounded by thick walls to absorb the radiation and neutrons, and, on account of the enormous amount of energy liberated by the nuclear disintegration of the ^{235}U , must also be cooled so that the internal temperature is maintained at 300—400°. The uranium isotope ^{235}U is contained in ordinary uranium to the extent of 0.7 % along with ^{238}U (and a very small amount of ^{234}U). This suffices for supplying enough neutrons for the conversion of ^{238}U . For this purpose the uranium must be extraordinarily pure, in order that impurities, which react more

readily than ^{238}U with neutrons do not act as neutron absorbers. The rare earths, which accompany uranium in nature, interfere more than anything else. Since such interfering elements are formed by the fission of ^{235}U , which occurs alongside the nuclear synthesis of ^{239}U from ^{238}U , the process is interrupted before all the ^{235}U is used up. The plutonium which is formed can be separated from the uranium by chemical reactions. For the preparation of plutonium, hundreds of kilograms of uranium were bombarded with neutrons from the cyclotron during several months in the summer of 1942. Pure plutonium compounds were thereby obtained by B. CUNNINGHAM and L. B. WERNER in September 1942. By the end of 1943, 1 mg of pure plutonium had been successfully obtained. By the following year considerable quantities had been manufactured.

Preparation of elements 95, americium, 96, curium, 97, berkelium and 98, californium. — Am and Cm have been obtained by the bombardment of ^{238}U and ^{239}Pu with helium ions of 40 million electron-volts. Their chemical properties were first investigated on radioactive tracers, but americium has since been obtained in weighable quantities. Latterly, evidence has been obtained for the preparation of elements 97 and 98—for which the names berkelium (Bk) and californium (Cf) have been proposed—in the bombardment of ^{241}Am and ^{242}Cm respectively with helium ions^{72a}.

Concerning the chemical properties of the trans-uranic elements. — In broad outlines, the following has become known about the chemical properties of the trans-uranic elements, which is of importance for the continuation of the Periodic System beyond uranium.

Neptunium can appear with the valencies 6, 5, 4 and 3. The lower states of oxidation are stabler than in the case of uranium, and oxidation to the higher valence states requires stronger oxidizing agents.

Plutonium likewise has valencies of 6, 5, 4 and 3. Trivalent plutonium is stabler than trivalent neptunium. Hexavalent plutonium forms plutonyl compounds isomorphous with the uranyl salts, but no ferrocyanide, since the ferrocyanide ion reduces hexavalent plutonium to the tetravalent state, which is the most stable state of oxidation for plutonium. Its compounds exhibit strangely different colours. Plutonium dioxide PuO_2 is a reddish brown. The hydroxide is precipitated with a pale-green colour from solutions of Pu^{IV} salts. The nitrate $\text{Pu}(\text{NO}_3)_4$ dissolves in nitric acid with a green coloration. The sulphate of tetravalent plutonium is a light-pink powder which dissolves in dilute acids with a pale-pink coloration. Distinguished by their low solubility are $\text{Pu}(\text{IO}_3)_4$, likewise a pale pink, and PuF_4 (like UF_4) which, however, is only precipitated with certainty in the presence of lanthanum salts. The soluble compounds of tetravalent plutonium are reduced to the light-blue trivalent salts by sulphur dioxide, hydroxylamine hydrochloride, hydrazine salts and also by iodides, but they are fairly

^{72a} S. G. THOMPSON, A. GHIORSO and G. T. SEABORG, *Phys. Rev.*, 1950, [ii], **77**, 838; S. G. THOMPSON, K. STREET (JR), A. GHIORSO and G. T. SEABORG, *ibid.*, 1950, **78**, 298.

quickly reconverted by atmospheric oxidation into tetravalent compounds. The chloride, perchlorate and sulphate of trivalent plutonium are readily soluble. The fluoride PuF_3 , like PuF_4 , is insoluble in dilute acids. Pu^{III} is oxidized at 60° by permanganate in acid solution beyond the Pu^{IV} stage to hexavalent plutonium. Of the plutonyl salts, the orange nitrate $\text{PuO}_2(\text{NO}_3)_2$ has been prepared ⁷³.

As far as is yet known, the stability of the trivalent state is still further enhanced relative to plutonium with the succeeding trans-uranic elements.

By reason of the chemical properties, it has been suspected that in the trans-uranic elements the O shell is being filled analogously to the filling of the N shell in the rare-earth group. It is even put forward as possible that this filling up of the O shell already commences from actinium onwards, and hence that the actinides should be classed along with the lanthanides ^{73a}. In this connection, however, it is necessary to point to a noteworthy difference, namely that the actinides can then be brought very much more easily than the lanthanides into a valence state higher than 3, whereas in the latter group tetravalence is pronounced only with cerium and praseodymium, as well as being hinted at in terbium, and invariably occurs along with a valency of 3. By contrast, it may not be overlooked that thorium is almost exclusively tetravalent. This speaks against the commencement with thorium of a series in which the *f* subgroup in the O shell is filled up, analogously to the filling up of the *f* subgroup in the N shell beginning with cerium (or likewise of the *d* subgroup of the M shell beginning with scandium). It therefore appears questionable whether the electrons in the outer shells of thorium may, otherwise than in the table on p. 272, be grouped as

O				P			Q
<i>s</i>	<i>p</i>	<i>d</i>	<i>f</i>	<i>s</i>	<i>p</i>	<i>d</i>	<i>s</i>
2	6	10	1	2	6	1	2

as has been suggested. However, if the analogy between the actinides and lanthanides is carried to its conclusion, then the structure of the O shell of element 95 will correspond to that of the N shell of the rare earth 63, namely europium: likewise element 96 will correspond to gadolinium with its seven *f* electrons. It is in line with this supposition that the names americium for element 95 and curium for element 96 were first proposed, in which in the one case Europe and America, and in the other the discoverer of the rare-earth minerals, GADOLIN, and the investigators of the radioactive elements, M. and P. CURIE, are placed in parallel.

However, this analogy cannot yet be held as completely certain. It needs to be supported not only by chemical arguments, but also by investigations

⁷³ B. G. HARVEY, H. G. HEAL, A. G. MADDOCK and E. L. ROWLEY, *J. Chem. Soc.*, 1947, p. 1010. The half-life period of ²³⁹Pu: G. T. SEABORG, *Chem. Eng. News*, 1945, 23, 2190. For further concerning the chemical properties of Np and Pu, see G. T. SEABORG and A. C. WAHL, *J. Am. Chem. Soc.*, 1948, 70, 1128.

^{73a} Evidence supporting this based on a number of different physical properties is discussed by Z. SZABÓ, *Phys. Rev.*, 1949, [ii], 76, 147.

of the spectra and magnetic properties. Until the latter are available, the question remains an open one. In considering the chemical properties of elements in groups VII and VIII, it must not be forgotten that these are by no means so strongly governed by the group number as in the case of elements situated in the other parts of the Periodic System. Thus, with rhenium, for example, the stage in oxidation corresponding to hexavalence is markedly more stable than in the case of hexavalent manganese. It accordingly appears completely possible that the lack of perspicuousness in the valence states of the elements in group VII and the adjacent group VIII, where the valency corresponding to the group number is to be found in only a very few compounds, is also extant in the trans-uranic elements. This renders it impossible to make any certain kind of extrapolation from the properties of the elements situated above them in the Periodic System. It might here be brought to mind that the elements rhodium and iridium, below which americium comes to be placed, are preponderantly trivalent.

The publication of the properties of the compounds of the trans-uranic elements which have been prepared to date, and the further extension of their chemistry will be awaited with interest from the standpoint of the chemist, for whom a knowledge of the electronic configuration of the outer shells is important. These elements with the highest atomic numbers deserve notice not only on account of the problems of the atomic nucleus, which problems are at the moment in the forefront from the point of view of interest.

10. Ortho and Para Hydrogen

The nuclear spin of the atoms comprising molecules is, apart from the single exception of hydrogen, without noteworthy influence on the properties of the molecule. As already mentioned, it makes itself noticeable solely in the hyperfine structure of the spectral lines, where its influence is then especially clearly seen in the case of molecules consisting of two identical atoms. It may then be shown⁷⁴, in a manner which will not be gone into more closely here, that an alternation of intensity must be present in the intensity curve of the various rotation bands, according to whether the nuclei have the same or opposed spins. The magnitude of the difference in the intensity depends upon the nuclear spin. For the nuclear spin $\frac{1}{2}$, as possessed by the hydrogen atom, the antisymmetric state of the nuclei possesses a "weight" three times as great as the symmetric, so that the intensities of the lines alternate in the ratio 3 : 1. For larger nuclear spins, the ratio is smaller. It was originally in 1924 that R. MECKE⁷⁵, on examining the not exactly lucid multilinear spectrum of hydrogen, had his attention drawn in this way to

⁷⁴ See, for example, A. EUCKEN, *Lehrbuch der chemischen Physik* I, p. 474 (2nd Ed., 1938).

⁷⁵ R. MECKE, *Physik. Z.*, 1924, **25**, 597; *Z. Physik*, 1925, **31**, 709. The correct interpretation based on the quantum theory was first given in 1927: W. HEISENBERG, *ibid.*, 1927, **41**, 239; F. HUND, *ibid.*, 1927, **42**, 93.

the difference in the "modifications" of the hydrogen molecule which are now designated as *ortho* and *para hydrogen*⁷⁶. Besides this, as had been discovered from other approaches, hydrogen also exhibited peculiarities in the variation of its specific heat at low temperatures⁷⁷ which were not then understood, but today are seen to follow directly from the fact that ordinary hydrogen is a mixture of *ortho* and *para hydrogen* in the ratio 3 : 1. The modification designated *ortho hydrogen* has spins the same in both of the atoms of its molecule, the *para* form having opposed spins. The differences caused by the nuclear spin are not limited here to the fine structure of the bands of the molecular spectrum, but are extended to other properties, exactly as also occurs with deuterium. Since *para hydrogen* has been successfully prepared pure, it is possible to make the differences evident by contrasting its properties with those of the ordinary mixture rich in *ortho hydrogen*. Pure *ortho hydrogen* has not yet been obtained.

The preparation of pure *para hydrogen* is possible because, on account of its small free energy, it is the only stable form at absolute zero. Ordinary hydrogen is an equilibrium mixture of the two modifications which corresponds to the equilibrium at high temperatures. This is scarcely different from that at room temperature. It can be shown theoretically that the ratio of *ortho* to *para hydrogen* cannot exceed the value 3 : 1, even at the highest of temperatures, and that consequently *ortho hydrogen* approaching purity cannot be obtained by the method of establishing equilibrium. In the absence of catalysts, the equilibria once reached at various temperatures are preserved, so that, by way of example, the boiling point of ordinary hydrogen, which is observed at -252.7° corresponds to the 3 : 1 equilibrium mixture and not to that in force at -252.7° , which would contain about 99.8 % *para hydrogen*. In the presence of a catalyst the equilibrium is very quickly reached, even at temperatures as low as this. After removal of the catalyst, the *para hydrogen* with its specific properties can be studied on its own, since in the absence of catalysts it remains for a long time unchanged, even at temperatures in the neighbourhood of 800° ⁷⁸. At high pressures, even at low temperatures, a change does set in which becomes noticeable within a few days⁷⁹.

The establishment of equilibrium is catalyzed by the following:

(i) Suitable metals, especially those which are hydrogenation catalysts and are able to release hydrogen as atoms, like platinum, nickel and iron; active charcoal at low but not, by contrast, at ordinary temperatures.

⁷⁶ K. F. BONHOEFFER and P. HARTECK, *Sitzungsber. Preuss. Akad. Wiss., Phys. Math.*, **1929**, p. 103. For *ortho* and *para hydrogen*, see the monograph by A. FARKAS, *Ortho-hydrogen, Parahydrogen and Heavy Hydrogen* (Cambridge, 1935).

⁷⁷ A. EUCKEN, *Sitzungsber. Preuss. Akad. Wiss.*, **1912**, p. 141. More recent investigations: A. EUCKEN and K. HILLER, *Z. physik. Chem.*, **1929**, **B 4**, 142. Theoretical interpretation: D. M. DENNISON, *Proc. Roy. Soc.*, **1927**, **A 115**, 483.

⁷⁸ K. F. BONHOEFFER and P. HARTECK, *Naturwissenschaften*, **1929**, **17**, 182; *Z. physik. Chem.*, **1929**, **B 4**, 113.

⁷⁹ A. EUCKEN and K. HILLER, *Z. physik. Chem.*, **1929**, **B 4**, 142.

(ii) Paramagnetic substances⁸⁰, like atomic hydrogen, free organic radicals, nitric oxide and nitrogen dioxide, all of which are paramagnetic on account of their unpaired electrons; also oxygen, which is likewise paramagnetic, and paramagnetic ions in aqueous solution, like Mn^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} and Cu^{2+} , but not the diamagnetic ion Zn^{2+} ; again, the ions of the rare-earth metals Pr^{3+} , Nd^{3+} , Sm^{3+} , Gd^{3+} , Er^{3+} and Yb^{3+} . The rate of conversion is proportional to the square of the magnetic moment of the substance acting as a catalyst.

The electric discharge also effects the establishment of equilibrium.

The temperature dependence of the equilibrium, which can be calculated theoretically from the difference in energy between the two modifications, and which is confirmed by experiment, is reproduced in the following table:

temperature ($^{\circ}K$)	20	40	80	120	273	∞
para H_2	99.82	88.61	48.39	32.87	25.13	25.00
ortho H_2	0.18	11.39	51.61	67.13	74.87	75.00

The difference between the cohesion properties of para hydrogen and ordinary hydrogen is illustrated by the vapour pressures at the triple point and at the boiling point of ordinary hydrogen, as well as by the melting points:

	13.95 $^{\circ}K$	20.39 $^{\circ}K$	m.p.
ordinary H_2	53.9 mm	760 mm	13.95 $^{\circ}K$
para H_2	57.0 mm	787 mm	13.83 $^{\circ}K$

The not inconsiderable differences in the specific heats⁸¹ and in the thermal conductivities⁸² — the values of these quantities are greater for para hydrogen than for ortho hydrogen — are employed in order to analyze mixtures of the two modifications⁸³. In principle, the different magnetic properties could also be used to this end. Para hydrogen with its opposed nuclear and electron spins is diamagnetic, whereas ortho hydrogen, in which it is also true that the electron spins are opposed, has nuclear spins which have the same sense for both atoms and is paramagnetic.

⁸⁰ L. FARKAS and H. SACHSSE, *Z. physik. Chem.*, 1933, **B 23**, 1; 19. Theory: E. WIGNER, *ibid.*, p. 28.

⁸¹ A. EUCKEN and K. HILLER, *Z. physik. Chem.*, 1929, **B 4**, 142; K. CLUSIUS and K. HILLER, *ibid.*, p. 158.

⁸² H. SENFTLEBEN, *Z. physik. Chem.*, 1929, **B 4**, 169.

⁸³ See, for example, A. FARKAS, *Z. physik. Chem.*, 1933, **B 22**, 344.

CHAPTER V

METHODS FOR INVESTIGATING CHEMICAL BONDING

1. The Spatial Content of Matter, Structure and Chemical Bonding

(i) General

The kind of chemical bonding linking the atoms in matter is reflected in the properties. It is not *bond type* alone which determines the properties, the spatial arrangement of the atoms or *structure* also playing a part. Only the two together, which may be included in the term *constitution*, ultimately determine the properties. Conversely, therefore, unambiguous conclusions concerning the chemical bonding or the structure can only be drawn when the kind of influence on the properties exerted by one of the two factors — which, moreover, need not be independent of one another — is clear. Many properties, like the magnetic properties, for example, may frequently be to a great extent independent of the structure, and are then in consequence especially suited for the determination of the type of bonding. With a knowledge of structure, one would expect, basically speaking, to be able to make inferences regarding the chemical bonding from the most varied properties. In reality, with the methods which make use of observations of particular properties as a means of investigating the chemical bonding, very varied degrees of success are encountered. The deepest insight is obtained with those methods which concern themselves directly with the valence electrons: but also with the help of those methods which allow of no direct statement concerning the activity of the valence electrons, valuable indications of special states of bonding as well as of structural peculiarities can be obtained. Of these methods, one, the thermochemical or, still more generally, the thermodynamical, will not be discussed here. It provides, it is true, valuable information concerning the energy relationships predominating in the formation of chemical compounds and also concerning the strengths of bonds: but, on account of its purely energetic basis, it is never able to make any disclosure concerning the nature of the chemical bonding or of the interaction of valence electrons and nuclei. If we would learn something about these points, we must take a path which many wished to tread earlier when inquiry was being made into the cause of chemical affinity between atoms, and not be satisfied with results which provide an energetic measure of the affinity of chemical processes, even if they refer to the union

of two atoms. Without wishing to misinterpret the significance of these thermodynamical measures of affinity, we will now leave them on one side in order to make a methodical approach — if not in a direct manner, then by feeling our way forward in various directions according to a plan — to the operation of affinity between atoms in the chemical bond.

But before we turn to those methods which touch directly upon the chemical bonding, the preliminary task will be to assess the value of a method which, without penetrating any deeper into the bonding relationships, can nevertheless provide the above-mentioned indications of special conditions of bonding or structural peculiarities. It is the *spatial-chemical method* which, broadly speaking, has set itself the task of investigating the connections between density or specific volume and constitution. In attempting to utilize it for investigating chemical bonding or structure, we grasp only a part of the task which it has been set. That it does not lead far need not surprise us, since the mechanical spatial requirements of a substance are in the last resort linked in an extraordinarily complicated manner with the state of bonding of the atoms and their steric arrangement. But it nevertheless hints at many interrelationships. A knowledge of the density of a substance is moreover essential for the exploitation of other methodical studies relating intrinsically to the investigation of the chemical bonding and having as prerequisite a knowledge of the number of atoms or molecules present in a given space, this being obtained from the *density* and the atomic or molecular weight.

As a preliminary method, "spatial chemistry" offers an advantage not to be underrated.

Of the various properties which depend on the kind of chemical bonding, the *specific volume* of substances is especially simple to determine experimentally. However, as already mentioned, the theoretical connections between specific volume and chemical bonding are unusually involved. In addition to this, the type of bonding linking the atoms is not the only factor which determines the space they occupy. One does not learn from the specific volume, therefore, anything which directly concerns the type of bonding, the characteristics of which can be inferred only indirectly from the particulars relating to the way in which the volume is occupied. No information concerning these particulars is obtained by this means. In making inferences of this kind, it must each time be borne in mind that the spatial requirements are determined to a large extent by the *structure*, as well as by the chemical bonding. Observed regularities or peculiarities in the spatial content can thus also be conditioned by a structural factor. Consequently, in any given case a special examination of the question regarding which factor is determinative is invariably necessary.

The influence of structure on the specific volume is already seen in the change in volume which takes place during the process of melting. On melting, the nature of the bonding between the atoms may be preserved. In

such cases the influence of structure is immediately apparent. In other cases, however, chemical bonds which exist in the crystal lattice are changed on melting, as, for example, when silicates are fused. Both factors then play a part. The structural factor vanishes in the case of liquid substances. It is therefore useful to distinguish between the molecular volumes of liquid and solid substances. With liquid substances, as long as the melts consist of molecules, the *intermolecular forces* play a decisive rôle. Hence, from the densities of these molecular melts, conclusions concerning the kinds of bonding between the atoms within the molecule can be drawn only to the extent that the intermolecular forces have different magnitudes for different kinds of bonding. On the other hand, it is not permissible, in comparing the molecular volumes of liquid substances with various kinds of bonding, to identify the sense of the change in volume with the sense of the change in distance between the atoms within the molecule. It is thus not correct to assert, for example, that in compounds containing a carbon-carbon double bond the doubly bound carbon atoms are further apart from one another than they are when singly bound, simply because the atomic volume of carbon in unsaturated compounds is larger than in saturated compounds.

On account of the different coefficients of expansion¹ possessed by different substances, the choice of reference temperature is not unimportant when comparing molecular volumes. For liquids¹, the boiling point under the same pressure comes into consideration, this being usually at approximately the same proportion of the critical pressure p_c . Thus, at atmospheric pressure the boiling point is about two-thirds the critical temperature, that is, $T_b = \sim \frac{2}{3}T_c$ (GULDBERG's rule)². According to the law of corresponding states, liquids on boiling are in such a corresponding state. The influence of intermolecular forces on the volumes, which makes itself so strongly noticeable when comparing the latter at the same temperature, is to a large extent eliminated by comparison at the boiling points.

For solid substances, the coefficient of expansion is determined by the increase in vibration of the lattice particles about their equilibrium positions that occurs with increasing temperature. Basically, therefore, from the coefficient of expansion one must also be able to learn something concerning the strength of the chemical bonds linking the units in the lattice. Yet the relationships are so involved — for crystals which are not regular, the expansion coefficients differ in different directions — that it has not been

¹ Under certain circumstances, the coefficient of expansion provides information concerning the state of bonding within a melt. Melts which consist mainly of ions possess decidedly smaller coefficients of expansion than melts which consist preponderantly of molecules. Interionic forces are stronger than intermolecular. Thus the halides of K, Rb, and Cs have almost exactly the same coefficients $\alpha = 4 \times 10^{-4}$, whereas BeCl_2 and other halides, whose melts conduct electricity either not at all or only badly, all have coefficients above 8×10^{-4} (W. KLEMM, *Z. anorg. Chem.*, 1926, 152, 295).

² C. M. GULDBERG, *Z. physik. Chem.*, 1890, 5, 375.

possible to utilize them for the said purpose³. A comparison of the volumes at absolute zero appears to be indicated, since at this temperature lattice vibrations cease and their influence is eliminated. For the majority of comparisons, however, it makes no fundamental difference whether they are made with respect to absolute zero or ordinary temperatures. The conversion of measurements made at high temperatures to absolute zero is naturally subject to uncertainties, but these are not large, especially when the coefficients of expansion have been determined over a large temperature range. And even when such determinations are lacking, there are rules with the help of which such conversions can be made with satisfactory precision⁴.

For inorganic substances, which for the most part have relatively high melting points, comparisons of molecular volumes in the liquid state only rarely come into consideration. We may therefore confine ourselves completely to the molecular volumes of solid substances⁵.

(ii) The Spatial Content of Simple Salts, especially the Alkali Halides

The way in which the spatial content is used for investigating the constitution of solid substances goes back to the oldest procedure of discovering connections between constitution and physical properties. This consists of finding additive properties whose values can be calculated by summing up atomic constants in the same way as the molecular weight can be obtained by the addition of atomic weights. With a strictly additive property like the molecular weight, the influence of the chemical bonding is completely excluded, that is, for properties other than that of mass it is to be regarded as constant within the scope of the compounds under comparison. Deviations from additivity point to constitutional peculiarities, that is, to changes either in the bond type or in the structure. As far as the volume of solid substances is concerned, experience soon showed for the example of the crystalline salts that, at least to a certain degree of approximation, it could be spoken of as an additive property. The following rounded numbers⁶ for the molecular volumes of a few alkali and silver halides illustrate this point:

KCl 37	NaCl 26.5	AgCl 26
KBr 42	NaBr 31	AgBr 29
KI 52	NaI 40	AgI 41

The differences between the sodium and potassium salts or the sodium and silver salts with the same anions are about equally large; likewise the differences of the chlorides, bromides and iodides with different cations. SCHRÖDER, who was the first to notice this, denoted these regularities by the term *parallelosterism*.

³ Concerning the application of the coefficients of expansion of liquids, see p. 307, footnote 1.

⁴ W. BILTZ, *Raumchemie der festen Stoffe*, pp. 10—12 (Voss, Leipzig, 1934).

⁵ A treatment is provided by W. BILTZ in *Raumchemie der festen Stoffe*.

⁶ With the numbers given by SCHRÖDER in 1859, which are now recognized to be inexact, the additivity is somewhat better than with those reproduced here.

When in connection with these results an additivity of volumes of the lattice particles is postulated (concerning the dimensions of which nothing is learnt from the numbers, since only differences can be represented), particles of constant volume are employed as models for the structural units in the lattice. With this volume they are then able to fit without gaps into the various lattices only if they are plastic and very easily deformable. Such a model is different from another which is much in use today, and that especially for heteropolar compounds. This model is that of a rigid sphere of constant radius. In the lattice these spheres make contact, the distances between the centres being the lattice distances. Here, therefore, the radii of the spheres and not the volumes are additive, for, according to the relative sizes of the spheres and the kind of lattice structure, interstices of varying magnitudes remain vacant. The postulates of additivity of volumes and radii are thus mutually exclusive and are not to be combined with each other⁷. With certain assumptions concerning the structure — *e.g.*, the assumption of a face-centred cubic lattice — it is possible both for ideal and for approximately realized additivity of radii to calculate in which direction the deviations from additivity of volumes lie and *vice versa*⁸.

Experience teaches that additivity is strictly realized neither with radii nor with volumes. Sometimes the one fits the observational data better and sometimes the other. In the case of the alkali halides, as is now known, the additivity of radii holds to a considerably greater degree of approximation⁹, and the same is true of many other classes of heteropolar compounds. The inferences to be made therefrom, which admit of important conclusions concerning the crystal structure, will be referred to elsewhere (Chapter VIII). It is however fitting, in spatial-chemical considerations, to follow the historical development and proceed from the alkali halides. Research was obliged to take this course, for until structural analysis by X-rays was available nothing could be known about lattice distances. In one case, which will be mentioned shortly, spatial-chemical considerations even enabled a prediction concerning structural peculiarities to be made, this being confirmed soon afterwards by X-ray analysis. Even today, now that numerous lattice distances are accurately known, spatial-chemical considerations are not to be regarded as obsolete, although, on account of the success in considerations of lattice distances with the help of the spherical model, they may appear to be forced into the background. Now, as then, they constitute a valuable supplementary approach.

How large the influence of bond type on the space occupied may be is shown not by comparing the alkali halides with one another, but by placing

⁷ Concerning this, see (among others) V. M. GOLDSCHMIDT, *Neues Jahrb. Min. Geol.*, 1928, **A**, **Suppl.** 57, 1119.

⁸ W. ROSEMAN and K. MEISEL in W. BILTZ's *Raumchemie der festen Stoffe*, pp. 270—285.

⁹ This is shown by a comparison of the tables relating to molecular volumes in this chapter, p. 310, and lattice distances in Chapter VIII, 4, (i).

them alongside the alkali metals themselves. The atomic volume of metallic potassium with 45 cm³ is *larger* than the molecular volume of potassium chloride with 37 cm³. It follows from this that it is not possible merely to ascribe a certain amount of space to an atom of an element. This formerly really surprising discovery is easily understood today. In elementary potassium the metallic bonding in the lattice is effected by a remote valence electron; in potassium chloride such is not present, since it has been given up by the potassium to the chlorine, whereby much less spacious ions result. These, on account of their opposing charges, approach one another much more closely than do the potassium atoms in the metal.

In contrast to this large effect which depends upon the presence of quite different types of bonding, only the finer differences in structure and bonding are reflected in the volume relationships on comparing the alkali halides, which are all heteropolar, with one another, as also with other salts. As already mentioned, the molecular volumes of the alkali halides are not strictly additive. Nevertheless, a volume relationship valid to a very good degree of approximation exists, FAJANS and GRIMM¹⁰ having derived such from more recent observations, the results of which are reproduced in the accompanying table.

	F	Δ	Cl	Δ	Br	Δ	I
Li	9.19	10.34	20.03	4.37	24.40	7.52	31.92
Δ	5.07		6.47		6.97		8.09
Na	14.76	11.74	26.50	4.87	31.37	8.64	40.01
Δ	7.90		10.27		10.99		11.92
K	22.66	14.11	36.77	5.59	42.36	9.57	51.93
Δ	4.34		5.58		5.98		6.46
Rb	26.5	15.85	42.35	5.99	48.34	10.05	58.39
Δ	+6.3		-0.15		-0.44		-0.79
Cs	32.8	9.4	42.2	5.7	47.9	9.7	57.6

With the exceptions of the caesium halides and of rubidium fluoride, all the molecular volumes have been derived from density measurements at -184° and are valid for -184° ¹¹. In the case of RbF only an X-ray measurement of the density at 20° is available, whose numerical value (27.0) has been recalculated for -184° . For the caesium halides the densities at 20° have been measured: the molecular volumes derived from these are given here uncorrected for 20° , since they originate from different authors and are therefore in any case not strictly comparable with the other figures. A correction to -184° would give the still smaller values 32.2, 41.1, 46.7 and 56.2 respectively, whereby the exceptional positions of the chloride, bromide and iodide would appear to be still more accentuated.

¹⁰ K. FAJANS and H. G. GRIMM, *Z. Physik*, 1920, **2**, 299.

¹¹ F. A. HENGLEIN and G. HÄHNEL, *Z. physik. Chem.*, 1925, **117**, 292.

The numerical values given in the table do not agree with those of the table given by FAJANS and GRIMM, who utilized older and less precise measurements throughout. As far as the uniformity of the measurements are concerned, the numerical material used by them is less homogeneous than that given here. As is seen, the differences between the potassium and sodium halides, for example, or between the fluorides and chlorides are not constant, as they would have to be for volume additivity. However, they can be made constant if the observed molecular volumes are multiplied by a factor which for one cation is collectively valid for the series of its halides. If the potassium halides are arbitrarily chosen as the starting point for the comparison, in which the factor for them is made equal to unity, the observed relationship can be expressed by a linear equation, and is therefore termed the *linear relationship*:

$$V_{KX} - aV_{MX} = b \quad \text{or} \quad V_{KX} = aV_{MX} + b.$$

In this, KX signifies the series of potassium halides, MX those of the halides of the other alkali metals, and a and b constants which are different and characteristic for each alkali metal. These constants are not independent of one another, but the larger the value of b , the larger that of a also. For the rubidium halides, where b has the value of only about 4 cm³, a is almost equal to 1, that is, for a comparison of potassium and rubidium, volume additivity holds to a really close approximation.

Graphically, the linear relationship is best represented so that the molecular volumes of the potassium salts are plotted as abscissa and those of the salts of the other alkali metals as ordinate. In this way, straight lines are obtained, the slopes of which differ according to the value of a . For the value $a = 1$, that is, for the potassium halides themselves, it is inclined at an angle of 45°. Parallel lines would mean volume additivity. This representation for the halides can also be extended to other salts of the alkali metals, which, as in the diagram shown for potassium and rubidium salts (Fig. 32), combine to give excellent linear relationships.

Conversely, the linear relationship has also proved to be valid, not only for the halides of the alkali metals, but also for halogen compounds collectively, including organic halides¹² (Fig. 33).

The *caesium halides* constitute a striking exception, which moreover immediately becomes apparent on a critical inspection of their molecular volumes as compared with those of the other alkali halides. Whereas quite generally the molecular volume of a halide otherwise increases with increasing atomic weight of the cation or anion, the molecular volumes of caesium chloride, bromide and iodide are *smaller* than those of the corresponding rubidium halides. In contrast, caesium fluoride, as was to be expected, possesses a larger molecular volume than rubidium fluoride. The linear relationship holds within the series CsCl, CsBr, CsI, but not for the complete

¹² W. BILTZ, *Z. anorg. Chem.*, 1921, 115, 241; 117, 84.

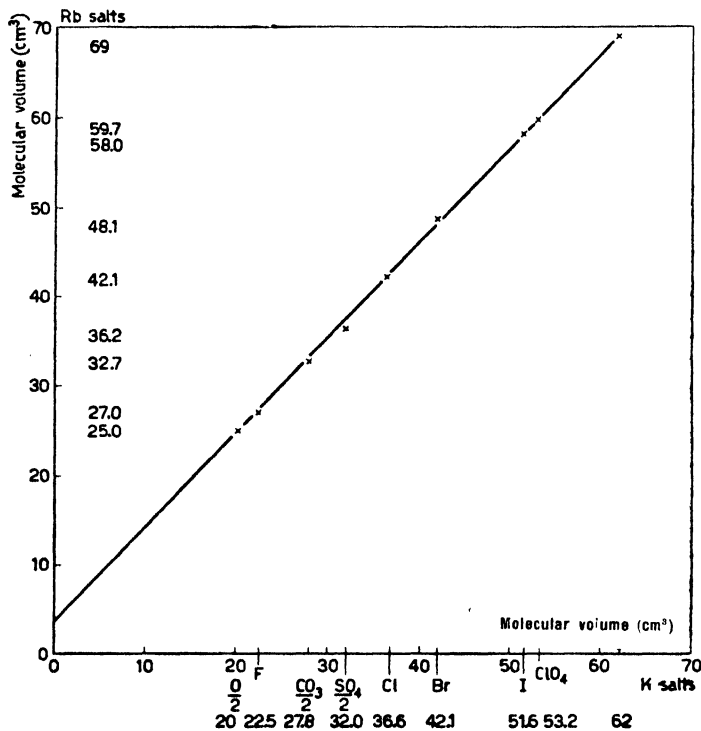


Fig. 32. Molecular volumes of potassium and rubidium salts

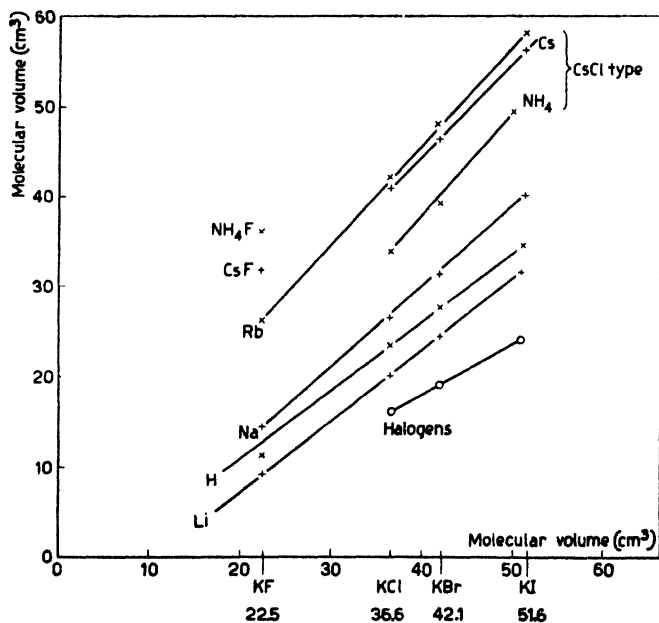


Fig. 33. Linear relationships for the molecular volumes of halides of the alkali metals, ammonium and hydrogen

series of caesium halides, in which CsF constitutes an irregularity. From this, FAJANS and GRIMM¹³ concluded that CsCl, CsBr and CsI must possess a crystal structure differing from that of all the other alkali halides, and one with a closer packing of the ions. X-ray analysis has confirmed this prediction¹⁴. The modifications of CsCl, CsBr and CsI stable at ordinary temperatures form body-centred lattices in which each ion possesses the co-ordination number 8. The remaining alkali halides, including CsF, have face-centred lattices with co-ordination number 6 for the ions. The failure of the linear relationship for ammonium fluoride and ammonium chloride is, as in the case of the caesium halides, to be attributed to a change of crystal structure.

The cause of the closer packing of ions in the caesium and ammonium halides is the particular *crystal structure* and not a different kind of bonding. With their pronounced saltlike character, which is in no way to be differentiated from that of the other alkali halides, this is self-evident. Influence of the bond type, on the other hand, shows up in the kind of linear relationship through the magnitude of the factor a which it contains. In the graphical representation, this is reflected in the slope of the line¹⁵. This may be seen especially clearly on comparing the isomorphous sodium and silver halides, whose crystal structures are the same. For the silver halides, as also for the halides of other monovalent elements in the subgroups — Cu^I, Tl^I, Hg^I (omitting HgF) — the linear relationship is realized very well; but the molecular volume changes on passing from the fluoride to the iodide considerably less than in the case of sodium, as the following table shows:

	V_0	Δ		V_0	Δ
NaF	14.7	}	AgF	17.7	}
NaCl	26.3		AgCl	25.5	
NaBr	31.2		AgBr	28.3	
NaI	39.8		AgI	(33.7)	
			AgI _{hexagonal}	41.5	

25.1 16.0 in mixed crystals

Of the fluorides, the sodium salt has the smaller volume, for all the other halides, the silver salt. The ordinary β iodide of silver, since it possesses another crystal structure, may not be used for comparison: if it were, the influence of structure would almost compensate that of bond type.

The cause of the different degrees of change in volume from fluoride to iodide in the sodium and silver salts is to be sought in the following. The halide ions become increasingly polar with increasing atomic weight. (Concerning the physical significance of the concept of polarizability and its measurement, see pp. 340, 348.) The silver ion, with its shell of eighteen electrons, is more strongly polarizable than the sodium ion. Consequently, a considerable reciprocal influencing of cation and anion occurs in the silver halides which, on account of the small polarizability of the fluoride ion, is

¹³ *Op. cit.* (footnote 10), p. 304.

¹⁴ W. P. DAVEY and F. G. WICK, *Phys. Rev.*, 1921, [ii], 17, 403.

¹⁵ W. BILTZ calls the tangent of the angle of slope the *Dehnungszahl*.

only slight for the fluoride but increases sharply in passing to the iodide. The typical saltlike character in the silver halides consequently becomes more and more lost as the atomic weight of the halogen increases, so that finally the iodide normally crystallizes not in the rock-salt type, but in a hexagonal lattice related to the wurtzite structure, one which is not found among typical salts (cf. Chapter VIII, 5, (ii)). Proceeding hand in hand with increasing interaction of cation and anion, a "fusing" is observed, that is, a diminution of the space occupied by the cation and anion. It thus comes about that the silver halides from the chloride onwards exhibit an increasingly large minus increment in spatial content with respect to the sodium halides, although, in actual fact, as a comparison of the fluorides shows, the silver ion possesses a larger volume than the sodium ion.

If the bond type in a series is so extensively homopolar that an interchange of co-ordination lattice containing ions or deformed ions as structural units for a molecular lattice sets in, this is immediately to be noticed in the molecular volume by a breaking down of the linear relation. As examples of this, the halides of the elements of groups III and IV come into consideration, of which the fluorides, chlorides and bromides of the elements in group IV have been selected.

Molecular volumes in cm^3 extrapolated to absolute zero

	C	Δ	Si	Δ	Ti	Δ	Zr	Δ	Ge	Δ	Sn	Δ
F_4	~ 43		47.7		~ 40		~ 37		46.4		~ 40	
Cl_4	74.6	31.6	83.1	35.4	86.1	46	82.5	45.5	84.3	36.9	89.7	49.7
Br_4	88.4	13.8	98.8	15.7	102	15.9	—		~ 100	~ 16	105.6	15.9

While the jump from chloride to bromide is everywhere practically of the same magnitude, namely about 16, in the jump from fluoride to chloride two different magnitudes are clearly to be distinguished, large jumps of over 45 for titanium, zirconium and tin, and small jumps of about 35 for carbon, silicon and germanium. The last-named elements conform to the linear relation, since all the halides of these elements form molecular lattices. For the others, a change in the lattice structure occurs between the fluoride and chloride, this being coupled with a change in the state of bonding. This change, which for the fluoride means an enhanced tightness of bonding in the lattice, is also noticeable in the trend of the boiling points. For C, Si and Ge, the fluoride boils lower than the chloride, for Ti, Zr and Sn, higher. For further concerning the state of bonding in these compounds, see Chapter VII, 3, (iii).

(iii) Space Increments

In the case of heteropolar compounds, for which approximately the same linear relation holds and for which the additivity of volumes is realized to a certain degree of approximation, *space increments* can be assigned to the individual ions, from which the molecular volumes of the salts can be approximately calculated by addition. These increments do not follow directly from the molecular volumes, which only provide their differences:

$$\text{Li}/\text{Na} \sim 5.7; \text{Na}/\text{K} \cdot 9.5; \text{K}/\text{Rb} \cdot 4.0; \text{Rb}/\text{Cs} \cdot 5.9; \text{Rb}/\text{NH}_4 \cdot -0.5; \\ \text{Cl}'/\text{Br}' \cdot 5.3; \text{Br}'/\text{I}' \cdot 9.1.$$

For the derivation of the — approximate — absolute values, additional limitations are needed, exactly as in the calculation of ionic radii, which is executed with the assumption of additivity of radii (Chapter VIII, 4, (i)). These restrictions are furnished by comparing the dimensions of ions with similar electron envelopes but different numbers of charges: the ion with the greater charge must have the smaller volume. From this it necessarily follows that

$$\text{Li}' < \text{H}' ; \text{Na}' < \text{F}' ; \text{K}' < \text{Cl}' ; \text{Rb}' < \text{Br}' ; \text{Cs}' < \text{I}'.$$

If, now, a salt is considered in which cation and anion have the same number of electrons, *e.g.*, LiH and NaF, a sharing of the available space equally between the two partners must be regarded as too generous towards the cation. Halving the molecular volume thus provides an upper limit for the ionic volume of the cation. Since, for example, the molecular volume of NaF is 14.7 cm³, the volume of the sodium ion must be less than half of this, namely 7.4. Since the volume of the lithium ion cannot be less than zero and the Li'/Na' difference is 5.7, the value for the ionic volume of Na' must lie between the two values specified. In this way, the following approximate space increments are arrived at for the ions of the alkali metals:

$$\text{Li} \cdot 0-2; \text{Na} \cdot 6.5; \text{K} \cdot 16; \text{Rb} \cdot 20; \text{Cs} \cdot 26; \text{NH}_4 \cdot 19.5.$$

For the alkaline-earth metals:

$$\text{Be} \cdot 0; \text{Mg} \cdot 2; \text{Ca} \cdot 6.5; \text{Sr} \cdot 11; \text{Ba} \cdot 16.$$

For anions¹⁶:

$$\text{F}' \cdot 9.5; \text{Cl}' \cdot 20; \text{Br}' \cdot 25; \text{I}' \cdot 34; \text{O}'' \cdot 11.$$

Although these figures represent only approximate values which are not even constant, they provide a clear picture of the spatial relationships. To be sure, it may appear strange that the spatial requirements for the lithium and beryllium ions must, as a lower limit, be set at zero. This becomes understandable if the considerations of spatial chemistry are supplemented by considerations of models formed from rigid spheres, as suggested by the lattice concept. Between anionic spheres which contact one another, in the event that these are sufficiently large, enough empty space remains

¹⁶ The dependence of the anionic increment on the valency of the partner, which is to be ascribed to polarization phenomena, is neglected here. The stated values refer to salts with monovalent cations: with divalent cations, values smaller by about 2% are obtained.

Conversely, there are also closely packed lattices, for which the values deviate on the low side, as in Al_2O_3 (corundum) with 25.7 ($\gamma\text{-Al}_2\text{O}_3$ (Chapter VIII, 9, (viii)), by contrast, 29.8 !), TiO_2 (rutile) with 18.9 (anatase already 19.7) and MnO_2 with 17. Generally speaking, however, there is a mean closeness of packing of the oxygen atoms which is governed by the oxygen atoms themselves, by virtue of which the equality of molecular volumes is approximately realized.

The frequently observed similarity in molecular volumes of different oxides of the same element, which was noticed as early as 1840 by F. AMMER-MÜLLER¹⁹, has its origin only partly in a spaciousness of the lower oxide. In the main, it is usually to be ascribed to a smaller space requirement of the more highly charged cation in the higher oxide. A few examples are:

Cu_2O	23.1	Ce_2O_3	47.9	Tl_2O	44
2CuO	24.0	2CeO_2	47.8	Tl_2O_3	45.2
Ag_2O	31.6	Pr_2O_3	46.7	PbO	23.1
2AgO	32.5	2PrO_2	46.6	$\frac{1}{3}\text{Pb}_3\text{O}_4$	24.7
				PbO_2	24.6

The various volumes have been reduced to absolute zero.

(iv) The Spatial Content of Complex Compounds. Penetration Complexes

Important conclusions concerning the state of bonding in complexes have been drawn from a comparison of the volumes which the complexly bound atoms or groups occupy in complex binding and in the isolated state. In this, as has already long been known, it has resulted that the water in hydrated salts takes up almost the same volume in every case, this being smaller than in ordinary ice and, as W. BILTZ has remarked, almost agreeing with the volume of the densest ice modification VI. The state of bonding of the water molecules in the hydrates of salts is thus almost the same as in the closest-packed ice modification. The same state of bonding will also prevail in ordinary ice, but from the point of view of spatial chemistry this does not become noticeable, since the influence of the exceptionally spacious crystal structure of ice I (Chapter VII, 2, (ii)) masks this similarity. In the hydrates of acids and bases, the space demanded by the water is appreciably smaller than in the salt hydrates²⁰. Here lies a clear indication of a special type of bonding of the water, this forming the hydroxonium complex OH_3^+ with a proton, and possibly also in like manner a complex with the hydroxyl ion.

For the saltlike ammoniates, in contrast to the hydrates, considerable differences may exist in the spatial requirements of ammonia²¹. In the ma-

¹⁹ Poggendorffs *Ann. Physik*, 1840, **49**, 341.

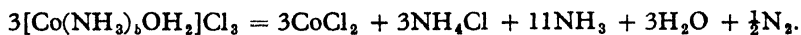
²⁰ E. MOLES and M. CRESPI, *Z. physik. Chem.*, 1927, **130**, 337.

²¹ Measurements: W. BILTZ, *Z. anorg. Chem.*, 1923, **130**, 131; G. BØDTKER-NAESS and O. HASSEL, *Avhandl. Norske Videnskaps-Akad. Oslo, Mat.-nat. Klasse*, 1933, No. 7.

majority of cases, to be sure, the volume of the complexly bound ammonia is the same at about 20 cm^3 ²², and consequently almost equal to that of ammonia itself, namely 19.6 cm^3 ²³. In the various amines of calcium chloride, for example, NH_3 has the following molecular volumes: $\text{CaCl}_2 \cdot \text{NH}_3$ 19.88; $\text{CaCl}_2 \cdot 2\text{NH}_3$ 19.39; $\text{CaCl}_2 \cdot 4\text{NH}_3$ 19.66; $\text{CaCl}_2 \cdot 6\text{NH}_3$ 19.63²⁴. But in the typical complex amines, as in the hexamines of cobalt and chromium in particular, it is considerably smaller with only 17 cm^3 ²⁵. This has the striking phenomenon for consequence that the complex amines of di- and trivalent cobalt, as also those of di- and trivalent chromium, are equal in volume, although the salts of the trivalent metals possess one anion more, e.g.:

$[\text{Co}(\text{NH}_3)_6]\text{Cl}_2$	156.9 cm^3	$[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$	156.4 cm^3
Br_2	171.6	Br_3	171.3
I_2	198.0	I_3	197.3
$[\text{Cr}(\text{NH}_3)_6]\text{Br}_2$	182.8	$[\text{Cr}(\text{NH}_3)_6]\text{Br}_3$	183.2

The kind of bonding of the ammonia in the amines of trivalent cobalt and chromium — not of iron, there being no equality of volumes for $\text{Fe}(\text{NH}_3)_6^{2+}$ and $\text{Fe}(\text{NH}_3)_6^{3+}$ — must therefore be a special one. A smaller volume for ammonia is paralleled by an increase in strength of the chemical bonding, as is also shown by the chemical behaviour of the amines. The voluminous amines permit a controlled removal of the ammonia molecules and, with respect to their stability, can be compared with one another by studying their thermal degradation or their equilibrium pressure of ammonia²⁶. The dense amines, on the other hand, possess no equilibrium vapour pressure, but on heating undergo with difficulty only an *irreversible* decomposition. For the corresponding aquo-amines, no pressure of ammonia, nor for that matter of water, can be determined. Thus, for example, aquopentamine cobaltic chloride decomposes irreversibly according to the following equation:



It is noteworthy that the ease of decomposition does not depend on the valency of the central atom, for, in contrast to $\text{Co}(\text{NH}_3)_6^{3+}$ and $\text{Cr}(\text{NH}_3)_6^{3+}$, the voluminous $\text{Fe}(\text{NH}_3)_6^{2+}$ ion is unstable and gives up its ammonia even more readily than the amines of the divalent metals. These and yet other

²² W. BILTZ and E. BIRK, *Z. anorg. Chem.*, 1924, **134**, 128 (from pycnometric measurements). More recent measurements from densities determined by X-rays are given in W. BILTZ's *Raumchemie der festen Stoffe*, p. 334. A certain dependence of the NH_3 volume on the nature of the anion as also on the peculiarities of the very unstable amines like $\text{Ba}(\text{NH}_3)_8^{2+}$ is disregarded here. Concerning this, see W. BILTZ, *Raumchemie der festen Stoffe*.

²³ W. HEUSE, *Z. physik. Chem.*, 1930, **A 147**, 273.

²⁴ L. J. GILLESPIE and H. T. GERRY, *J. Am. Chem. Soc.*, 1931, **53**, 3967.

²⁵ W. BILTZ, *Z. anorg. Chem.*, 1927, **164**, 249.

²⁶ The articles of W. BILTZ on this subject are in the main essentials summarized in *Z. anorg. Chem.*, 1923, **130**, 93. The literature comprising the numerous articles of F. EPHRAIM as far as the year 1923 is collected together by H. REIHLEN in R. F. WEINLAND's *Einführung in die Chemie der Komplexverbindungen*, p. 483, footnote 1 (2nd Ed., 1924).

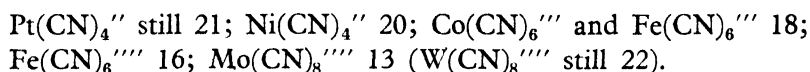
examples show not only how the spatial-chemical and energetic approaches supplement each other²⁷, but also how both are obliged to come to a halt at the same place; for, concerning the cause of the difference in bond type, the spatial content naturally provides no information. For such information, comprehensive physical measurements, in this instance especially magnetic (p. 396), must be applied to the state of bonding itself. Nevertheless, the special spatial position of the ammine-complexes of the type represented by the $\text{Co}(\text{NH}_3)_6^{3+}$ ion (luteo type²⁸) has led to the expression *penetration complex* for such complex compounds (p. 58). The small spatial requirements of the complexly bound groups are governed by the inclusion of an electron pair in the electron envelope of the central atom. Penetration complexes which are distinguished by their exceptional compactness also occur among the *complex cyanides*²⁹. The compact cyano-complexes, in consequence of the firmer binding of the cyano groups to the central atom, are more stable than the voluminous cyano-complexes. Here, however, the state of affairs is less simple than in the case of the amines, inasmuch as the molecular volume of the cyano group is subject to variation or, as has been expressed in other words by W. BILTZ, the cyanide ion, being a highly polarizable ion, is "very soft". This, however, does not comprehend all the peculiarities. In the simple heteropolar cyanides of the alkali metals, the volume of the cyanide ion with about 20 cm³ is fairly small and about equal to that of the chloride ion. In cyanides of the heavy metals it is appreciably larger, for example, 23 cm³ in AgCN and as much as 30 cm³ in $\text{Fe}(\text{CN})_2$. The mutual polarization of the ions, which in $\text{Fe}(\text{CN})_2$ is certainly carried to a point where an ionic lattice and a heteropolar compound may scarcely be spoken of any longer, thus leads in this case to an increase in the volume occupied, which is so large that it cannot be combined with peculiarities in the lattice structure. The effect thus lies in precisely the opposite direction to that for the silver halides, where the smaller slope of the lines representing the linear relationship indicates a reduction in the volume of the partner relative to the alkali halides. This becomes understandable only on returning to the electronic configuration of the cyanide ion, which corresponds to that of the nitrogen molecule (p. 420). If the symmetry of its electron cloud is disturbed through electrons being withdrawn on one direction, a discrete ion is no longer under consideration, so that the delicate interaction of electrons which leads to the stable N_2 configuration is brought into disorder. The electron cloud is thereby loosened, and demands more space in consequence. For this reason, the volume of the cyano group, even in the highly stable cyano-complexes $\text{Ag}(\text{CN})_2$,

²⁷ This mutual supplementing and stimulation of two lines of research, for which certainly, in accordance with theoretical knowledge, approximately the same limit must be drawn, receives expression in numerous articles of W. BILTZ, which he surprisingly names *Beiträge zur systematischen Verwandtschaftslehre*. They are based, as the title implies, essentially on a limitation of knowledge, which is the outcome of the thermodynamical definition of chemical affinity (p. 34 ff).

²⁸ From *luteolus*, yellowish. The $\text{Co}(\text{NH}_3)_6^{3+}$ ion is yellow.

²⁹ W. BILTZ, *Z. anorg. Chem.*, 1928, **170**, 161.

and $\text{Au}(\text{CN})_2'$ — if for Ag and Au the space increments derived from compounds which are not strongly heteropolar are inserted — is with 26 cm^3 larger than in the simple cyanides. In the quite exceptionally stable complexes, however, the volume of the cyano group, even though one electron pair of the N_2 shell it contains is much in demand because of bonding to the central atom (p. 396 ff), shrinks on occasions far below that of the free cyanide ion:



With these figures it is however to be remembered that, in their derivation, volumes have been employed for the ions regarded as the central atoms which have been assumed to be invariable, these having been estimated in part with a certain arbitrariness not to be avoided in the calculation of space increments. There can, however, be no doubt that strong contractions occur in these cyanides, in consequence of which the cyanide ion is changed in complex bonding to a much greater degree than, for example, the halide ions in the complex halo-acids, in which the volumes appear to be, though somewhat, only slightly diminished³⁰. Information concerning the peculiarities of the chemical bond in those cyano-complexes which correspond to penetration complexes is preferentially obtained from magnetic measurements.

It is also worthy of note that the small space increment for CN is only to be found in the heteropolar alkali salts of the complex cyanides and not in the salts of the heavy metals³¹: for example, such is found in $\text{K}_4\text{Fe}(\text{CN})_6$ but not in $\text{Zn}_2\text{Fe}(\text{CN})_6$ and $\text{Ni}_2\text{Fe}(\text{CN})_6$. This indicates yet another kind of bonding in the latter. In actual fact, X-ray studies have shown for a number of such ferrocyno- and ferricyano-complexes of the heavy metals that no discrete $\text{Fe}(\text{CN})_6''''$ and $\text{Fe}(\text{CN})_6'''$ ions exist in their lattices, but that a network of metal atoms linked up via the cyano groups into a three-dimensional lattice is present. Consequently, as has already been amplified in Chapter III (p. 151 ff), the cyano group is here in demand for chemical bonding on two sides, namely that of its carbon and that of its nitrogen atom. It is hence not surprising, in view of this dual claim, if its electron cloud is likewise loosened up relative to the uninfluenced complex ion so as to demand more room, in the way already depicted for the unidirectional influencing of the cyanide ion in cyanides which are not strongly heteropolar³².

³⁰ In this connection, see the table on p. 336 of W. BILTZ's *Raumchemie der festen Stoffe*.

³¹ W. BILTZ, *Z. anorg. Chem.*, 1928, **170**, 161.

³² The stability of the cyano-complexes can be determined by electrometric titration with hydrochloric acid, in which, if the complex is not very stable, a potential jump is to be observed at the equivalence point, as in the cases of $\text{K}_2\text{Hg}(\text{CN})_4$, $\text{K}_2\text{Cd}(\text{CN})_4$ and $\text{KMn}(\text{CN})_4$. HCN and the metal cyanide are formed thereby. $\text{KAu}(\text{CN})_2$ does not give such a jump, and shows itself to be completely stable towards HCl. J. BRIGANDO and P. JOB, *Compt. rend.*, 1946, **222**, 1297.

The examples cited suffice in order to show in what manner research in spatial chemistry can prepare the way for research into chemical bonding. They teach at the same time the limits which apply to it; and, by way of indication, the directions in which it needs supplementing by other methods have been variously referred to. These other methods, which make a direct attack on the problem of chemical bonding, will now be turned to.

2. Structure Analysis by X-rays

Various kinds of observations are required for a knowledge of the chemical bond uniting atoms. A complete description is associated with the following data:

- (i) distance between the nuclei;
- (ii) spatial arrangement of the valence electrons;
- (iii) strength of binding of the electrons;
- (iv) strength of binding of the nuclei;
- (v) behaviour of the valence electrons during perturbations.

In order to obtain these data, various methods of investigation are necessary which must be combined with one another. Under certain circumstances, a method which originally supplies the answer to only one question is also able, when sufficiently refined, to answer further questions. The methods mainly utilized are:

- X-ray analysis;
- X-ray diffraction;
- electron diffraction;
- conductivity measurements;
- dielectric measurements;
- refraction of light;
- absorption of light
- (a) in the visible and ultra-violet spectrum,
- (b) in the infra-red spectrum;
- RAMAN effect;
- magnetic measurements.

The *internuclear distance* is determined for crystalline substances by X-ray analysis, for gases by the diffraction of X-rays or electrons.

X-ray analysis not only supplies the geometry of the structures in the sense of the classical stereochemistry of VAN 'T HOFF, LE BEL and WERNER, but also gives, with the interatomic distances, the absolute dimensions in the sense of the lattice theory of crystals. This depends upon the fact that the interatomic distances in the lattice are commensurable with the wave-lengths of X-rays, so that interference phenomena may occur. Consequently, with X-rays of a known wave-length, it is possible to derive the lattice distances from the interference phenomena, as also conversely the

wave-length from known lattice distances. In principle, this is the same method as is employed for interference phenomena with visible light when either the number of lines in a diffraction grating and the distance between them is determined from a known wave-length, or conversely the wave-length of the light is calculated from the dimensions of the grating. The diffraction of X-rays by a crystal lattice differs from the diffraction of visible light by a line or cross grating only inasmuch as, in the crystal, one is dealing with a three-dimensional lattice. The consequence of this is that reinforcement of the incident X-rays by interference takes place only for very special orientations of the incident beam and the crystal layers with respect to each other. These orientations are given either by the LAUE equations, which correlate them with the interatomic distances a , b and c in the crystallographic axes, or by the BRAGG equation for the angle of reflection, which contains the distance d between the layers.

(i) LAUE's equations:

$$a(\cos \alpha - \cos \alpha_0) = h_1;$$

$$b(\cos \beta - \cos \beta_0) = h_2;$$

$$c(\cos \gamma - \cos \gamma_0) = h_3;$$

where α_0 = the angle between the incident rays and rows of atoms along the a axis, α = the angle between the diffracted rays and the rows of atoms along the a axis (β_0 , β and γ_0 , γ being the corresponding angles with respect to the b and c axes), and h = the order of the beam diffracted by the row of atoms, being expressible by a whole number.

Of the three angles which the direction of the incident and likewise diffracted rays make with the three crystallographic axes, only two can be independently chosen, since the angles at which these axes are inclined to one another are fixed by the crystal system. In general, therefore, with arbitrary angles of incidence, α_0 , β_0 and γ_0 , and monochromatic X-rays of wave-length λ , no diffracted beams will be observed. The values of h_1 , h_2 and h_3 must more frequently fulfil certain conditions if values of α , β and γ are to be found to satisfy the LAUE equations.

(ii) The BRAGG equation:

$$n\lambda = 2d \sin \vartheta,$$

where n = an integer = the order of reflection, and ϑ = the angle of reflection (2ϑ = the angle of diffraction).

Towards X-rays which fulfil these conditions, a lattice layer can act like a mirror, in which an incident ray of angle ϑ to the plane is reflected at the same angle. In order that a beam of X-rays may appear to be reflected in this way as a result of interference, it must for any given wave-length strike the lattice layer at a particular angle or, more generally, at a discrete number of angles for which $\vartheta = \sin^{-1} \frac{n\lambda}{2d}$ ($n = 1, 2, 3, \dots$). Alternatively, for a given angle it must possess a particular wave-length or, more generally, a

discrete number of wave-lengths for which $\lambda = \frac{2d \sin \vartheta}{n}$ ($n = 1, 2, 3, \dots$).

The derivation³³ of the BRAGG equation appears in essence to be simpler than that of the LAUE equations, since it deals with the concepts of reflection and interference of rays reflected by successive lattice layers. In reality, however, this simplification in the process of derivation stands in need of theoretical justification, and in this the LAUE equations must be employed as foundation in order to show that the diffracted rays may be treated as rays reflected at the plane of the lattice layer³⁴.

The equations of LAUE and BRAGG contain different parameters, since LAUE works with the lattice distances a , b and c along the crystallographic axes and BRAGG with the distances between the lattice layers in different directions. These latter distances are related to the interatomic distances along the axes by means of a simple relation given by the MILLER indices h , k and l for the planes corresponding to the lattice layers. From this, the following relationships result, these linking the numbers h_1 , h_2 and h_3 occurring in the LAUE equations with the order of the angle of reflection according to BRAGG³⁵:

$$h_1 = nh; \quad h_2 = nk; \quad h_3 = nl.$$

The LAUE equations give the conditions for interference by rows of atoms lying along and parallel to the crystallographic axes, that is, for simple lattices. If other types of lattices are under consideration, which can always be thought of as arising by superimposing simple lattices upon each other, then interactions arise between the diffracted rays from the individual simple lattices. By these interactions certain interferences may be strengthened, others weakened, and again others even completely quenched. From these differences in intensity, which differ according to the way in which the lattices are superimposed and the way in which the lattice positions are occupied by particular kinds of atoms, the space group to which the lattice belongs can be derived. For example, the following is true for the lattice of caesium chloride, in which two simple cubic lattices, the one of Cs⁺ ions and the other of Cl⁻ ions, are superimposed upon one another in such a way that, collectively (neglecting the difference between the two ions), a body-centred lattice results. According to the orders h_1 , h_2 and h_3 of the interferences in the directions of the three axes (h_1 , h_2 and h_3 , although n -fold MILLER indices, are frequently replaced by h , k and l , which are otherwise used

³³ The lucid derivation of the equations of BRAGG and LAUE, which is to be found in many text-books, will not be given here.

³⁴ The theoretical connection between the approaches of LAUE and BRAGG is treated in most books either not at all or only quite briefly. A thorough treatment is to be found in NIGGLI's *Lehrbuch der Mineralogie und Kristallchemie*, Part II.

³⁵ The very lucid derivation of this interrelation is to be found, for example, in J. M. BIJVOET, N. H. KOLKMEIJER and C. H. MACGILLAVRY, *Röntgenanalyse von Kristallen*, § 16 (Springer, Berlin, 1940). The practice of various methods of structure investigation is also given (LAUE photographs, rotating-crystal method of BRAGG, powder method of DEBYE and SCHERRER, among others).

for the set of indices without a common divisor), the rays diffracted by the Cs' ionic lattice and those diffracted by the Cl' ionic lattice may mutually reinforce or mutually weaken one another. The former happens when the *sum* of the orders of the interferences is an even number, and the latter when it is odd. For the rock-salt type, on the other hand, the individual lattices of the sodium and chloride ions respectively are no longer simple but already cubic face-centred lattices. Thus all interferences with so-called "mixed indices", whose orders are not either *all* even or *all* odd, disappear. The result of superimposing the two face-centred lattices (again neglecting the difference between the ionic species) would be a simple cubic lattice with cell dimensions equal to one-half of those for the separate lattices. In consequence, interferences with even orders here strengthen one another, weakening occurring with odd orders. Because of the absence of interferences with mixed indices, a cubic lattice of the rock-salt type can be immediately distinguished from the caesium chloride type of lattice, which belongs to a different space group.

Whereas a knowledge of the relative intensities of the interferences is not necessary for the identification of a simple lattice, such a knowledge is needed for deriving the space group of a complicated lattice. When various species of atoms are present, the individual nature of the atoms situated in the lattice positions receives expression in the mutual strengthening or weakening of the interferences arising from the superimposed lattices. In general, different atoms have different scattering powers, which are measured by the ratios of the square roots of the intensities of the incident and deflected X-rays. This scattering power is found to be proportional to the number of electrons in the atom or ion, provided the scattering is confined to small angles of deflection. (For larger angles, the spatial distribution of the electrons in the atom also plays a part — see later.) This influence of the scattering power of the atoms is demonstrated very beautifully on comparing lattices of the same space group, in which the lattice positions of the original simple lattices are occupied in the one case by atoms with two different powers of scattering and in the other case by atoms which scatter almost equally. Those interferences, for which a weakening occurs in consequence of the interaction of the lattices, will in the second case be practically extinguished. An instructive example is furnished by a comparison of NaCl and KCl, since the scattering powers of the potassium ion and chloride ion which contain the same number of electrons is almost the same, whereas for the sodium and chloride ions it is markedly different. In consequence, the interferences with odd orders, for which a weakening occurs with lattices of the rock-salt type, are to be seen in the case of sodium chloride, whereas with potassium chloride they have disappeared.

The original extensively simplified theory of diffraction phenomena for crystal lattices which leads to the LAUE and BRAGG equations — the *elementary theory of scattering by crystal lattices* — thus requires supplementing

to take account of the material nature of the centres of deflection. This is necessary, not only where the qualitative fact of interference must be made comprehensible, but also where the quantitative intensity ratios for the rays arising by interference become important. It is then no longer feasible simply to proceed as in the classical presentation of wave optics — in which each line on a diffraction grating is regarded as a disturbing barrier, this, according to HUYGHENS' principle, becoming the origin of a new wave — without enquiring into the kind of interaction of the radiation with the material of the diffracting lattice through which the new wave comes into existence ³⁶.

This necessity of extending the theory ultimately indicates that X-ray analysis is in the last resort able to lead further than simply determining the atomic distances within the crystal lattice; for, as soon as the cause of the deflection process is enquired into, it is immediately seen that it is not the interactions between the X-rays and atomic nuclei which effect the scattering, since these are minimal, but those between the X-rays and electrons. That it is possible to draw conclusions from these latter interactions concerning the positions of the atomic nuclei is due to the circumstance that, in the lattice, each atom is surrounded on all sides by other atoms, in consequence of which the electron cloud enveloping the atom is centrosymmetrically constructed, or at least almost so. As a result, in giving rise to interference phenomena it acts to a first approximation as a sphere, whose interaction with the X-rays can be thought of initially as originating from its centre, where the nucleus lies. A more refined consideration must of course take into account the extension of the electron clouds in space and ultimately the electron density, not only in the immediate surroundings of the nuclei, but also in the entire space to be found between them.

The structure of the electron cloud introduces an atomic-structure factor or, more briefly, *atomic factor* into the treatment. This might be given the more correct but less gainly title, *electron-distribution factor* ³⁷. In the limiting case, where the angle of deflection is zero, it is proportional to the number of electrons, and is, in addition, a function of the angle of deflection, for, on eventual increase of this angle, the phase differences which arise through the fact that the scattering electrons in an atom are not all in the same place come into operation. As long as the angle is small, these phase differences remain small, it being almost as if all the electrons were situated together. If the angle of deflection is increased, the electrons do not all work together so well, but, in consequence of the increasing phase difference, partly neutralize each other in their action, so that the power of

³⁶ This kind of disregard of the material aspect is wide-spread in the representation of classical mathematical physics. For example, in the description of the changes of motion during a collision between two material bodies, the physical way in which the transference of energy takes place on collision is not at all gone into.

³⁷ A. EUCKEN, *Lehrbuch der chemischen Physik*, Vol. I, p. 296, footnote 3 (2nd Ed., 1938).

scattering decreases. This drop in the power of scattering is so much the steeper, the more extended the electron cloud; for, the further the electrons lie apart, the sooner the phase difference governed by the angle of deflection makes itself noticeable.

The theory which takes into account the atomic factor, that is, the spatial distribution of the electrons in the atom or ion, also treats — exactly as does the *elementary theory of crystal scattering* — the centres of scattering as the origins of new waves which interfere according to HUYGHENS' principle. The material nature of the particles receives expression in this *theory of wave motion* as opposed to the elementary theory, in that the electron distribution differs according to the species of atom. On the other hand, the theory of wave motion does not touch upon details of interaction between X-rays and electrons any more than does the elementary theory. This is considered by the still more far-reaching *dynamic theory*, which acknowledges that an electron possesses a wave nature and is even able to absorb and emit radiation, that the radiating electrons interact and that a back coupling of the electrons with the primary radiation occurs. But, for the majority of cases, the theory of wave motion suffices. It breaks down, however, when the wave-length of the primary X-rays is not decidedly smaller than the shortest wave-length which the scattering electron can emit, and also for large ideally constructed crystals, as are frequently met with in diamond, calcite, quartz, zinc blende and, very occasionally, in rock salt and other substances. In ideal crystals, the radiation originating from the interaction of the radiating electrons operates in such a way that the formulae for the intensities are completely different from those that occur in the theory of wave motion. Accordingly, the interference patterns appear different from the usual. The dynamic theory can remain out of consideration as far as the interesting problems of evaluating the interatomic distances and electron distribution are concerned.

If, in the manner already discussed, X-ray analysis is pushed to the point where the observed intensities are related to the electron density as it varies from place to place in the entire space between the atomic nuclei, one is already on the path towards solving task (ii) mentioned at the outset of this section (p. 321), namely the determination of the distribution of the valence electrons. Since crystals are being investigated, this means studying the state of bonding of the atoms in the crystal lattices. This requires a FOURIER analysis of the density of the scattering electrons, the details of which method cannot be gone into more closely here. In the majority of cases it is linked with a very considerable amount of calculation. Naturally it requires a consideration of all the factors, not listed individually here, which exert an influence on the intensities of the diffracted X-rays, like the thermal motion of the atoms, for example. The density ρ of the scattering electrons appears as a periodic function of the distance d between two layers of the lattice in a particular direction, for example, along the z axis. It can be put in the following form:

$$\rho_x = A_0 + A_1 \cos 2\pi \frac{z}{d} + A_2 \cos 2\pi \frac{2z}{d} + \dots + A_n \cos 2\pi \frac{nz}{d}.$$

A_0 is the density which would occur for even distribution of the electrons between the two layers. The amplitudes of the FOURIER components $A_1, A_2,$ etc., must be related to the intensities of the deflections of different orders. This is easily possible, because the X-rays are deflected as if each FOURIER component scattered independently. Quite generally, one FOURIER component of period $\frac{d}{n}$ gives only one interference of the n th order. Proof of this cannot be given here, nor can a FOURIER analysis be carried out in detail to illustrate the ways in which the amplitudes A_1, A_2, \dots are evaluated. Since the last-named procedure is concerned with the development of a series which generally does not converge rapidly, intensity measurements up to a high order are necessary. The numerous intensity measurements must be very exact. In this connection, all factors influencing the intensities of the deflected X-rays, like the thermal motion of the atoms, for example, must receive consideration. In addition to precise experimental work, a great deal of calculation must be performed in a FOURIER analysis of this type. In return, however, apart from the electron distribution, the most precise data concerning the interatomic distances are obtained from it.

Only with the help of FOURIER analysis has it been possible to prove with complete certainty the existence of ions with closed electron shells in some of the alkali halides, in which the electron density has been found to be zero at a point between the metal and the halogen along the edge of a lattice cube. With the help of the usual X-ray analysis, in which the mutual intensification and weakening of the interferences of the lattices of the alkali and halide ions are drawn upon to determine the structure, the magnitude of the intensification and weakening is indeed given by the ratio of the scattering powers of cation and anion; but conclusions from this concerning the ionic character of the atoms occupying the lattice points can be drawn only with certain reservations. In the limiting case, namely for small angles of deflection, the powers of scattering are, it is true, approximately proportional to the electronic number of the lattice particle: in the very favourable case of lithium fluoride, the following ratios of strengthened to weakened intensities for occupation respectively by atoms and by ions would eventuate:

$$\begin{array}{l} \text{(for strengthening)} \\ \text{(for weakening)} \end{array} \left(\frac{\text{F} + \text{Li}}{\text{F} - \text{Li}} \right)^2 = \left(\frac{9 + 3}{9 - 3} \right)^2 = 4; \quad \left(\frac{\text{F}' + \text{Li}'}{\text{F}' - \text{Li}'} \right)^2 = \left(\frac{10 + 2}{10 - 2} \right)^2 = 2.25$$

Such differences in intensities are, in themselves, immediately recognizable. But, in consequence of the extension of the electron clouds in space, the scattering power diminishes with increasing angle of deflection, and so far it has proved possible to make measurements only at deflection angles for which the scattering power is considerably reduced. It is thus necessary

For flat organic molecules, the structural formula can be directly reflected in the diagrams reproducing the electron density in isobars, as in the cases of hexachlorobenzene ⁴¹ (Fig. 35) and phthalocyanine ⁴².

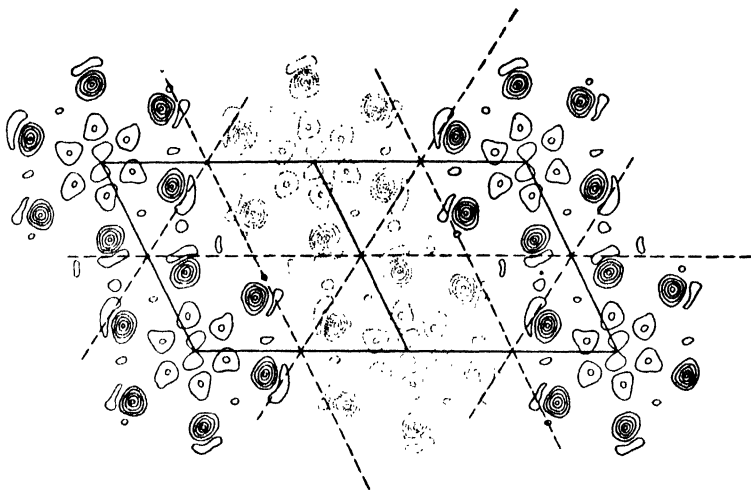


Fig. 35. Projection of the electron density of C_6Cl_6 on to the 010 plane.

3. Diffraction of X-rays and Electrons

(i) Diffraction of X-rays by Gases

In a monatomic gas, the diffraction of X-rays resulting from the spatial distribution of electrons about the nucleus is characterized by a continual fall in intensity with increasing angle of deflection, this being given by the factor for atomic structure. For monatomic gases, intensity maxima occur which owe their origin to an interference between the individual atoms or, more precisely, their electron clouds. From the intensity dependence of the scattered X-rays on the angle of deflection, the interatomic distances can be deduced by calculations and formulae (which will not be repeated here); and, moreover, the smaller the atoms, that is, the higher the density of electrons in their electron clouds, the more precise the deductions, since the interference maxima and minima become sharper accordingly. The atomic factors are needed for the calculations. For these, the values determined for the individual atoms or those calculated theoretically can be used with sufficient accuracy. The distances are not found directly from the diffraction intensities, but one proceeds in the opposite direction by commencing with molecular models based on different atomic distances, calculating

⁴¹ K. LONSDALE, *Proc. Roy. Soc.*, 1931, A 133, 536.

⁴² J. M. ROBERTSON, *J. Chem. Soc.*, 1936, p. 1195.

the diffraction patterns for these, and discovering which choice of atomic distances gives a pattern best agreeing with that observed. How exactly the calculated and observed values may match each other is illustrated by the intensity curve for carbon tetrachloride ⁴³ (Fig. 36).

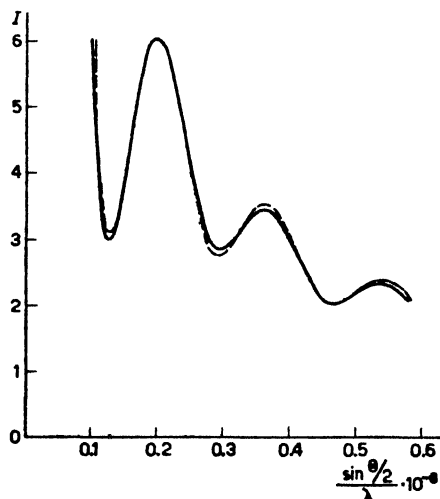


Fig. 36. Intensity variation with dependence on the angle of deflection in X-ray diffraction by carbon tetrachloride.

The determination of interatomic distances by X-ray interference in gases has today lost ground to the electron-diffraction method, among other reasons because the latter gives much greater scatter intensities and consequently demands a very much shorter period of illumination.

(ii) Electron Diffraction

On encountering matter, electrons can behave like electromagnetic radiation of a periodic nature and very short wave-length, and give rise to interference phenomena. In this, they work with a wave-length which is determined by their velocity c , their mass m and PLANCK'S quantum of action ($\lambda = \frac{h}{mc}$). This type of behaviour of electron beams analogous to that of X-rays was first unequivocally observed in 1927 by DAVISSON and GERMER ⁴⁴ on allowing electron beams to be reflected at the surfaces of single nickel crystals. For electrons of definite velocity, diffraction maxima in definite directions were thereby observed, these being dependent on the choice of surface. Later ⁴⁵, the experiment was carried out in a form corresponding

⁴³ W. VAN DER GRINTEN, *Physik. Z.*, 1933, **34**, 609.

⁴⁴ C. J. DAVISSON and L. H. GERMER, *Phys. Rev.*, 1927, [ii], **30**, 705; earlier and not necessarily conclusive experiments by DAVISSON and C. H. KUNSMAN date back to the years 1921 and 1923.

⁴⁵ For example, C. J. DAVISSON and L. H. GERMER, *Proc. Nat. Acad. Sci., U.S.*, 1928, **14**, 317.

to BRAGG's procedure for the angle of reflection in X-ray analysis. Beams of electrons of definite velocity were "reflected" only at quite definite angles as a consequence of the interference phenomena of the crystal. Likewise, other procedures imitating those employed for the production of X-ray interferences illustrate interference phenomena with electron beams.

Although electron interferences are completely similar in their outward appearance to X-ray interferences, the processes which give rise to them may not be equated, but, on account of the different kinds of interaction between matter and X-rays on the one hand and matter and electrons on the other, are different in nature. In the case of X-rays, it is the *electrons* which constitute an obstacle for these electromagnetic waves of short wavelength on striking matter, from which obstacle, according to HUYGHENS' theory of wave motion, the secondary waves which interfere with one another radiate. For electron beams, on the other hand, the *potential field* at the various points within the atom constitute the obstacle with which, as the origin of the interfering waves, the theory of wave motion is concerned. (To be sure, the dynamic theory also considers the wave nature of the scattering electrons in the atom, but this need not concern us here, since for ordinary purposes the theory of wave motion suffices, and that too under suppositions very similar to those made when dealing with X-ray interferences.) Since the potential field and the electron density in the atom have different forms, both the dependence on the angle of deflection and the intensities of the scattered radiation are completely different for the diffraction of electrons and X-rays. In particular, the strong potential field from the nuclear charge makes itself evident in the diffraction of electrons, whereas the influence of the nucleus is negligible in the diffraction of X-rays. This charge on the nucleus, on account of its positive nature, operates in the diffraction process in the opposite direction to the electron cloud. Consequently, in the equation giving the relationships between the angle of deflection ϑ and the ratio of the intensity of the radiation deflected at this angle to that of the primary radiation, a difference appears, namely that between the nuclear charge Z and the atomic factor. The relation is of such a kind that, with increasing angle ϑ , that is, with increasing order of diffraction, the intensity of the deflected electrons falls off much more quickly than in the case of X-ray diffraction. On the other hand, for small angles of deflection, the intensity relative to the intensity of the primary beam is very much greater, in consequence of the powerful action of the potential field originating from the nuclear charge. Consequently much shorter exposures are required for electron interferences than for X-ray interferences. Against this advantage for electron-diffraction photographs is the disadvantage that, because of the rapid drop in intensity, the interferences cannot be followed up to high orders. On account of the strong scattering for electrons, absorption is much stronger than for X-rays, so that for the LAUE type of exposure the electrons can only be allowed to pass through thin

cleaved plates of a crystal, or for exposures of the DEBYE-SCHERRER powder-method type only through thin layers of powdered crystals. Electron diffraction is thus a suitable method for investigating the structure of thin surface layers, *e.g.*, the oxide films of passive metals, since, because of the absorption, the deeper-lying layers do not come into play. X-ray interferences are effected with the additional action of the lower layers, and are by nature inapplicable for this purpose. Other differences in the exposures obtained by electron diffraction and X-ray interferences from crystals will not be touched upon further here. For crystals, X-ray exposures are preferred throughout for determining the structure and interatomic distances.

The reverse is true in the determination of interatomic distances in gaseous molecules. Here the electron-diffraction method has quite preponderantly received application. On account of the brevity of the exposure time, and also of the generally more simple apparatus, there is tolerance of the fact that the periodicity of the diffraction maxima and minima disappears⁴⁶ with increasing angle of deflection, this being due to the rapid diminution of the atomic factor. Only an intensity curve falling in steps is observed. From the position of these steps and their height it is possible by a special analysis procedure⁴⁷ to draw conclusions concerning the interatomic distances in the molecule. Alternatively, commencing with particular models of the molecule, the intensity curves expected for various atomic distances can be calculated in order to see for which assumptions these best agree with those found experimentally. As an example of the stepwise drop in intensity, the result of the photometric evaluation of an exposure for sulphur hexafluoride⁴⁸ is reproduced (Fig. 37).

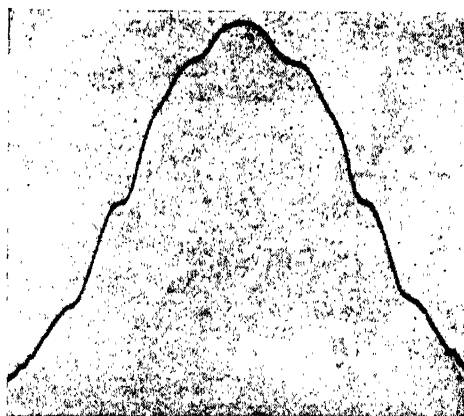


Fig. 37. Intensity curve for the diffraction of electrons by sulphur hexafluoride.

⁴⁶ These are usually present in the case of X-ray diffraction.

⁴⁷ L. C. PAULING and L. O. BROCKWAY, *J. Am. Chem. Soc.*, 1935, **57**, 2684.

⁴⁸ H. BRAUNE and S. KNOKE, *Z. physik. Chem.*, 1933, **B 21**, 297.

4. Conductivity Measurements

(i) Conductivity of Melts

The electrical conductivity of a substance can be either metallic or electrolytic and, by its nature, is able under certain circumstances to provide information concerning the state of bonding between the atoms. In this, it is necessary to distinguish between the conductivity of liquids and that of solids, since the kind of conductivity in the latter still depends upon factors connected with the state of order, these factors being without significance in melts.

The conductivity of *molten* inorganic compounds has been mainly investigated with the object of finding out whether electrolytes or non-electrolytes are being dealt with. To ascertain this is also important for an understanding of the reactivity, which is connected with the state of bonding. Frequently it is possible from the behaviour of a molten salt to make inferences concerning its crystalline state⁴⁹, which increases the importance of conductivity measurements on melts. To be sure, in compounds of complex structure like the silicates, the conductivity is so complex, depending upon various carriers of electricity which cannot be separated out, that inferences of this type become inadmissible and one must be content solely with a determination of the kind of conductivity. Also, when, as with the molten saltlike halides, the state of affairs is somewhat simpler, it is not possible to gather from the numerical value of the conductivity of melts which are good conductors very much more than the fact that they conduct electrolytically, since the ionic mobilities of cations and anions which come into the picture are connected with the ionic dimensions and viscosities of the melts in a not very perspicuous way. One has to be satisfied with the drawing up of a few empirical and not very precise rules⁵⁰. Only when the conductivity of an electrolytically conducting melt is relatively low is it possible to conclude that this is only partly to be attributed to electrolytic dissociation of the molten salt, as, for example, in the case of magnesium chloride, whose equivalent conductivity at the melting point is only half as much as that of the other alkaline-earth halides. Compared with this kind of differentiation between melts which are good electrolytic conductors, the jump to the melts which do not conduct or are almost non-conductors is extraordinarily large. Between magnesium chloride and beryllium chloride, for example, this is a matter of more than two powers of ten. Further details are provided in the tables which follow later.

Since a quantitative interpretation of the numerical values found for the conductivity has not so far been achieved, there is nothing further to say

⁴⁹ W. KOSSEL, *Z. Physik.*, 1920, 1, 395; G. VON HEVESY, *Kgl. Danske Videnskab. Selskab Medd.* III, 1921, No. 13; W. BILTZ, *Z. physik. Chem.*, 1922, 100, 52.

⁵⁰ See the compilation by W. BILTZ and W. KLEMM, *Z. anorg. Chem.*, 1926, 152, 285 (Table 5).

here concerning the theory of conductivity of melts. That the theory must take the degree of dissociation, ionic size and viscosity of the melts into consideration is seen from what has already been said. In practice, it is still of importance to decide the conditions under which the conductivities of the various substances are preferably to be compared. A conductivity referred either to the molecular volume V or to the equivalent volume $\frac{V}{n}$, in which n is the number of possible ions reduced by 1⁵¹, appears to be more suitable than the specific conductivity referred to 1 cm³. These quantities which are suitable for comparison are related to the measured specific conductivity κ in the following ways:

$$\begin{aligned} \text{molecular conductivity } \mu &= \kappa \cdot V \\ \text{equivalent conductivity } \Lambda &= \frac{\mu}{n} = \kappa \frac{V}{n} \end{aligned}$$

The choice of temperature for comparison is not simple, since, because of the oftentimes very different positions of the melting and boiling points, all substances cannot be measured at the same temperature. Furthermore, if one does not confine oneself to comparison within similar classes of compounds, the choice of a desirable temperature for comparison would be arbitrary because of the different temperature coefficients for the conductivity, which may even have different signs. Generally, the conductivity increases with the temperature, but there are exceptions such as HgI₂, InCl₃ and InBr₃, for example. According to the law of corresponding states, the boiling points would provide suitable temperatures for comparison, but for experimental reasons these must be eliminated. Similar fractions of the absolute boiling points would be admissible as corresponding temperatures, but inexact knowledge of the boiling points frequently stands in the way of their calculation. For this reason, BILTZ and KLEMM⁵², who are credited with the collection of an extensive amount of observational material for inorganic compounds, decided in the main for a comparison at the *melting points*, at which the measurements can usually be conveniently made.

The clearest comparison is accomplished on the basis of the Periodic System. The difference between electrolytes and non-electrolytes is everywhere so striking, that it is possible to draw a sharp dividing-line through the System separating the elements which form compounds of different bond type with the same partner. On the whole, a change in conductivity runs parallel with a change in volatility (Chapter VII, 3, (i)). Only in a few places, as in the forementioned case of magnesium chloride, is it necessary

⁵¹ For a discussion concerning the reliability of such a mode of reckoning, see W. BILTZ and W. KLEMM, *Z. anorg. Chem.*, 1926, **152**, 269; P. WALDEN, *Ostwald-Druckers Handbuch der allgemeinen Chemie* IV, *Das Leitvermögen der Lösungen* 1, p. 6 (Leipzig, 1924).

⁵² W. BILTZ and W. KLEMM, *Z. anorg. Chem.*, 1926, **152**, 267. See here also for a list of individual investigations (p. 268, footnote 2) and the results of other investigators (tables, p. 273 ff).

by reason of the conductivity to assume the presence of considerable quantities of undissociated molecules along with the ions.

From the abundant experimental data, the very completely investigated chlorides have been selected to illustrate the sort of results to which the procedure of conductivity measurement leads.

Equivalent conductivity of the chlorides at the melting point

Main groups

HCl $\sim 10^{-6}$						
LiCl 166	BeCl ₂ 0.086 *	BCl ₃ 0	CCl ₄ 0			
NaCl 133.5	MgCl ₂ 28.8	AlCl ₃ 15×10^{-6}	SiCl ₄ 0	PCl ₅ 0		
KCl 103.5	CaCl ₂ 51.9	ScCl ₃ 15	TiCl ₄ 0	VCl ₄ 0		
RbCl 79.2	SrCl ₂ 55.7	YCl ₃ 9	ZrCl ₄	NbCl ₅ $\kappa = 2 \times 10^{-7}$	MoCl ₅ $\kappa = 1.8 \times 10^{-6}$	
CsCl 66.7	BaCl ₂ 64.6	LaCl ₃ 29.0	HfCl ₄	TaCl ₅ $\kappa = 3 \times 10^{-7}$	WCl ₆ $\kappa = 2 \times 10^{-6}$	
			ThCl ₄ 16		UCl ₄ $\kappa = 0.34$	

* 35° above the melting point

Subgroups

CuCl 87.4 (422°)	ZnCl ₂ 0.02 (318°)	GaCl ₃ almost 0 (75.5°)	GeCl ₄ 0 (-49.5°)
AgCl 111.5 (455°)	CdCl ₂ 51.4 (564°)	InCl ₃ 14.7 (586°)	SnCl ₄ 0 (-33°)
	HgCl ₂ 25×10^{-4} (277°)	TlCl ₃ ? ($\sim 30^\circ$)	PbCl ₄ $\sim 2 \times 10^{-5}$ (-15°)
	Hg ₂ Cl ₂ * ~ 40	TlCl 46.5	SnCl ₂ 21.9
		InCl ** 130	PbCl ₂ 40.7
		InCl ₂ ** (In ₂ Cl ₄) 29	

* 20° above the melting point under pressure

** Extrapolated to the approximate boiling point 550°, at which the value calculated for InCl₃ is 17. Concerning the peculiarities for the indium halides, see W. KLEMM, *Z. anorg. Chem.*, 1926, 152, 260; 262.

(ii) Conductivity of Crystalline Substances

For crystalline substances, there exists either an electronic conductivity or an electrolytic conductivity, or, alternatively, the substances are insulators. The conduction of electricity effected by electrons can be either metallic in type, and decrease with increasing temperature, or correspond in type to that of the so-called semi-conductors, for which the conductivity increases with increasing temperature.

Otherwise than for melts, the presence or absence of a conductivity is not in itself a proof of a particular state of bonding for crystals. Crystals of the heteropolar salts which consist of ions, *e.g.*, of the alkali halides, are mostly excellent insulators, precisely like crystals with homopolar bonding between the atoms. In the lattices of the typical salts, the ions are so firmly held in their places, that even at temperatures in the neighbourhood of the melting point, they are unable to wander under the influence of an electric field. The extremely minute diffusion velocities of ions in crystals, as can be ascertained for inhomogeneous mixed crystals among others, also bear witness to the stability of the lattice positions. The minute velocities of diffusion and generally extraordinarily small conductivities⁵³ which are observed depend, moreover, not on the movement of ions in the ideal lattice, but are a consequence of disarrangements in the lattice, in which the ions do not find themselves in the lattice positions to which they belong. It is especially at the boundaries of two contacting crystal blocks that such faults in the arrangement or even gaps in the lattice occur (concerning this, see Chapter XI, 7).

Also for crystals which possess an appreciable electrolytic conductivity, the latter is to be attributed to disorders of this kind⁵⁴. Under certain circumstances these disorders can assume exceptional dimensions, in that, even in the individual crystal blocks, the occupation of lattice positions is irregular. Examples of such extreme disorders, which may be linked to the presence of a good electrolytic conductivity, are provided by the regular modification of silver iodide stable above 146° (α silver iodide) and the modification of silver sulphide stable at high temperatures (α silver sulphide). In the case of α silver iodide, the mobility of the silver ions thus effected

⁵³ Calculation of the velocity of self-diffusion from the conductivity for NaCl, and measurements for PbCl₂ with the help of radioactive lead as indicator: G. VON HEVESY, *Sitzungsber. Akad. Wiss. Wien, Math.-nat. Kl. IIa*, 1920, **129**, 549. Ag in Ag₂Te: G. VON HEVESY and W. SEITH, *Z. anorg. Chem.*, 1929, **180**, 150. Ag in α -Ag₂S: C. TUBANDT, R. REINHOLD and A.-L. NEUMANN, *Z. Elektrochem.*, 1933, **39**, 227. Measurements of the diffusion of Ag⁺ in Cu₂S and Cu⁺ in Ag₂S (*Platzwechselfusionskonstanten*): C. TUBANDT, H. REINHOLD and W. JOST, *Z. anorg. Chem.*, 1928, **177**, 265; W. JOST and H. RÜTER, *Z. physik. Chem.*, 1933, **B 21**, 48; H. BRAUNE and O. KAHN, *ibid.*, 1924, **112**, 270; *Z. Elektrochem.*, 1925, **31**, 576. See also W. JOST, *Diffusion und chemische Reaktionen in festen Stoffen* (Steinkopff, Dresden and Leipzig, 1937).

⁵⁴ Concerning this, see C. WAGNER, *Z. physik. Chem.*, 1933, **B 22**, 181; 1936, **B 34**, 309; C. WAGNER and E. KOCH, *ibid.*, 1936, **B 32**, 439; C. WAGNER, *Z. angew. Chem.*, 1936, **49**, 738.

in the lattice attains to such a point, that it is a better conductor below its melting point than in the molten state. Its lattice is constructed⁵⁵ in such a way that the silver ions are housed irregularly in the 30 largest spaces in a cubic body-centred lattice of lattice distance 2.18 Å formed by the iodide ions. In the elementary body, which contains two iodide and two silver ions, the latter are statistically distributed between the 42 possible positions. The lattice is really preserved by the iodide ions, the silver ions behaving like a liquid interpenetrating the iodide lattice. The transition from the hexagonal modification of silver iodide stable below 146° — in which the silver ions are held firmly in their lattice positions — to the regular can consequently be represented as if the silver lattice breaks up at 146° and, as it were, “melts” within the iodide lattice. The lattice structures of α silver sulphide and α cuprous sulphide are similar⁵⁶.

Hexagonal (β) silver iodide possesses a normally constructed lattice of a type similar to the wurtzite lattice. It therefore does not show the peculiarities of α silver iodide. In consequence of the exceptional mobility of the silver ions present only in the latter, the conductivity at the point of transition of the β to the α form jumps 3700-fold.

For α silver iodide, the structure of the lattice with the mobile silver ions effects the flow of an electric current in such a way, that only silver ions wander. This one-sided electrolytic conduction⁵⁷, in which only the cation wanders, is characteristic of all electrolytically conducting crystals. That in reality a pure electrolytic conduction is under examination, is proved by the applicability of FARADAY's law.

In spite of a similarity in lattice structure, α silver sulphide behaves otherwise than α silver iodide in conducting electricity. In the pure state, it is a metallic conductor⁵⁸. In its lattice, it is true, the silver ions are not so mobile as in α silver iodide, for, above the transition point with β silver sulphide (179°), although statistically distributed in the spaces of the sulphide lattice, they are held quite firmly in these spaces. Only above 400° do they become as mobile as already happens at 146° in the silver-ion “liquid” (or “gas”) of α silver iodide. (The melting point of α -Ag₂S at $812 \pm 10^\circ$ ⁵⁹ also lies considerably above that of α -AgI at 526°.) But the difference in behaviour towards an electric current is not explained by this alone. It is rather to be sought in the fact that, in pure Ag₂S, a small proportion of the silver atoms are present not as monovalent Ag⁺ ions but as divalent silver, in consequence of which excess electrons are present. These, as conducting

⁵⁵ L. W. STROCK, *Z. physik. Chem.*, 1934, **B 25**, 441; 1935, **B 31**, 132; *Z. Krist.*, 1936, **A 93**, 285.

⁵⁶ P. RAHLFS, *Z. physik. Chem.*, 1936, **B 31**, 157.

⁵⁷ This was already observed by M. FARADAY, and likewise by W. HITTORFF. The latter also recognized the difficulties of electrochemical measurements on solid metal sulphides (cf. α -Ag₂S below): *Poggendorffs Ann. Physik*, 1851, **84**, 1.

⁵⁸ C. WAGNER, *Z. physik. Chem.*, 1933, **B 21**, 25; **B 23**, 469; C. TUBANDT and H. REINHOLD, *ibid.*, 1934, **B 24**, 22.

⁵⁹ K. FRIEDRICH and P. SCHOEN, *Metallurgie*, 1908, **5**, 23; 50.

electrons, take care of the transport of the current. Many sulphides whose metals can occur in several valence states possess metallic conductivity originating from the same cause. In the lattice of a sulphide, the metal can yield up more electrons than corresponds to its valence state, the sulphur binding only the number of electrons corresponding respectively to its low valence state, according to which valence state the compound is stoichiometrically composed. This will be more thoroughly discussed in another connection, namely in the discussion of the non-stoichiometrically composed oxides and sulphides (Chapter X, 6, (ii)).

If, however, the α silver sulphide is not quite pure Ag_2S , but contains a slight excess of sulphur — or, more correctly, a slight deficiency of silver (Chapter X, 6, (ii)) — with respect to the formula Ag_2S , the metallic conductivity is greatly decreased⁶⁰, in that the sulphur present in more than stoichiometric proportion binds the electrons of that small fraction of silver atoms which participate in divalence⁶¹. This fact contributed in causing α silver sulphide at first to be erroneously spoken of as a purely electrolytic conductor⁶², preparations of reduced metallic conductivity simulating through secondary processes a conformity to FARADAY'S Law⁶³.

In addition, however, there are also crystals in which, as the non-observance of FARADAY'S law shows, a metallic conduction of electricity occurs simultaneously with an electrolytic, the proportion of the two types of conduction becoming modified with the temperature. Consequently, it is possible for a crystalline substance to conduct almost entirely electrolytically within one temperature region, and practically only in a metallic manner within another. This is the case for one of the three modifications of cuprous iodide, which is solely a metallic conductor below 240° and solely an electrolytic above 390° . The two other modifications conduct only electrolytically⁶⁴. β silver sulphide is likewise a mixed conductor⁶⁵. At 0° it conducts purely electrolytically; with increasing temperature and current density, it is partly transformed into an electronic conductor up to the point where the proportion is approximately 21% electronic and 79% ionic conduction at 179° ⁶⁶, at which temperature the transition to α silver sulphide succeeds.

Whereas the existence of metallic conduction points to the presence of mobile electrons as in metals, and thereby to a type of bonding which is at

⁶⁰ C. TUBANDT and H. REINHOLD, *Z. Elektrochem.*, 1931, **37**, 589; *Z. physik. Chem.*, 1931, **Bodenstein Memorial Vol.**, p. 874.

⁶¹ This explanation appears to be more correct than the mechanical explanation of L. W. STROCK (*Z. physik. Chem.*, 1935, **B 31**, 132), in which sulphur atoms of radius 1.04 \AA are supposed to "block" the gaps in which the silver ions of radius 1.13 \AA are situated.

⁶² C. TUBANDT and M. HAEDICKE, *Z. anorg. Chem.*, 1927, **160**, 297.

⁶³ C. WAGNER, *Z. physik. Chem.*, 1933, **B 21**, 25; 37; 42; **B 23**, 469; W. JOST and H. RÜTER, *ibid.*, 1933, **B 21**, 48.

⁶⁴ C. TUBANDT, E. RINDTORFF and W. JOST, *Z. anorg. Chem.*, 1927, **165**, 195.

⁶⁵ C. TUBANDT and H. REINHOLD, *Z. anorg. Chem.*, 1927, **160**, 222.

⁶⁶ For further information, see also C. TUBANDT, S. EGGERT and G. SCHIBBE, *Z. anorg. Chem.*, 1921, **117**, 39; C. TUBANDT in GEIGER and SCHEBL'S *Handbuch der Experimentalphysik*, Vol. XII, p. 408 (1932).

least closely related to metallic bonding, the existence of electrolytic conduction cannot, by way of contrast, be regarded as proof for a decidedly ionic bonding; for, all other experimental data show, as instanced by the silver halides in consequence of the greater deformability of the silver ions (cf. p. 313), that there are no compounds as strongly heteropolar as the alkali halides, which are as good as non-conductors in the crystalline state. Indeed, silver iodide, owing to the strong deformability of both of the ionic species it contains, accordingly stands on the border-line between heteropolar and homopolar bonding. Also in silver bromide⁶⁷, which likewise behaves only as an ionic conductor, the existence of a transition type only just below the melting point is apparent from the fact that, commencing with the regular lattice of the rock-salt type, 16 % of the silver ions have wandered out of the octahedral spaces of the lattice formed by the bromide ions into the tetrahedral spaces, which signifies the beginning of a transition to the zinc-blende or wurtzite type. It is known that the bond type approximates here more closely to homopolar bonding than in the rock-salt lattice (cf. Fig. 164, Vol. II: octahedral and tetrahedral spaces in the rock-salt lattice).

5. Dielectric Measurements

(i) Dipole Moments

Important as dielectric measurements on electrically insulating materials are in practice in many cases, such measurements rarely yield observational material which can be utilized for probing into the state of bonding. To be sure, by such measurements something is learnt simultaneously about the electrical conductivities of the respective substances that permits inferences to be made concerning the possible presence of ions which govern the conductivity. Measurements of this type, having the conductivity as their aim in order to determine the polar nature of chemical bonds, have been employed particularly by W. BILTZ on halides (see p. 334). In addition, the measured dielectric constants of liquids as well as of solid substances offer, as a whole, an extensive collection of material still almost entirely in need of a theoretical interpretation. Although, for example, it is possible from their molecular structures to predict that water and hydrogen cyanide will possess high dielectric constants, the unusually high observed values of 81 and 115 respectively could not, as to their magnitude, have been foreseen; that is to say, it is still not possible to derive a quantitative relationship between the dielectric constant on the one hand and the structure and bond types within the molecule on the other. Likewise the considerable drop in dielectric constant to 3.2 on the freezing of water can be related only quantitatively to the loss of mobility of the water molecules in the lattice. The dielectric constant is a measure of the ability of a substance to orientate its smallest particles — molecules or atoms, or the electrons bound in these — in an electric field.

⁶⁷ C. WAGNER and J. BEYER, *Z. physik. Chem.*, 1936, **B** 32, 113.

In this, various factors co-operate which simply cannot be disregarded, unless the orientation of these particles succeeds independently or at least nearly independently of each other. This prerequisite is realized neither in liquids, where because of the close packing one molecule influences its neighbours, nor in crystals, for which, in addition, different dielectric constants in different directions must be reckoned with whenever crystals are being considered which do not possess a regular symmetry. On the other hand, it is realized for the molecules of a *gas*, and — with certain assumptions — also in the case of dilute solutions. The orientation of an isolated molecule in an electric field takes place because it is a system of electrical charges, that is, it consists of a positive nucleus and negative electrons. These charges are not linked absolutely rigidly to one another, but, under the influence of an electric field, can be displaced, that is, the molecule can be *polarized*. An external field can also have an orientating action, in that within the molecule the electrons are slightly displaced relative to the nucleus in the direction of the field, whereby an *induced dipole* arises in which the centres of gravity of the positive and negative charges do not coincide. The induced dipole arises independently of the position of the molecule with respect to the space co-ordinates and always in the field direction. The orientation thus does not extend to the molecule as a whole, but only to the charges within the molecule. If the unaffected molecule is centrosymmetrically constructed with the centres of gravity of its positive and negative charges coinciding, this intramolecular orientation effect is the only one. If, however, the molecule is in some way unsymmetrical, so that from the outset it is a dipole, then the orientation of this permanent dipole in an electric field is an additional factor, the field tending to twist the molecule into the direction of its lines of force. Thermal motion disturbs this tendency to orientate. With a dipolar molecule, therefore, there are two factors in operation, the intramolecular displacement polarization and the orientation polarization. For this reason, unsymmetrical dipolar molecules are easier to orientate than molecules of high symmetry, and the substances consisting of dipolar molecules consequently possess in general relatively high dielectric constants. The dielectric constant of a substance is thus in the general case determined by the *polarizability* and by the polarity of its component molecules. Hence the dipolar character of a molecule cannot be derived from the magnitude of the dielectric constant alone, unless a very high value is under consideration; for it is well within the bounds of possibility that a non-polar but easily polarizable molecule is, under certain circumstances, more readily orientated in an electric field than a weakly polar but difficultly polarizable molecule. On the other hand, the two effects, namely orientation by polarization and orientation of a permanent dipole, can be kept separate by virtue of a different temperature-dependence. The former, as an intramolecular phenomenon, is in first approximation independent of temperature, since the tightness by which the electrons are held may be regarded as practically constant

within not too great a range of temperature, and since the polarization always occurs in the field direction, independently of the orientation of the molecule. With respect to this orientation, however, there is a very appreciable dependence on the work which must be performed to reorientate a permanent dipole in the field, the thermal motion of the molecules acting against this reorientation. Consequently, the effect which rests upon the orientation of permanent dipoles is temperature-dependent.

The connection between the dielectric constant and the state of bonding in a molecule is thus a dual one. On the one hand there is the polarizability, which is a measure of the firmness by which the bonding electrons are held in their positions, and on the other the symmetry of the charge distribution. The two influences can be separated if the temperature-dependence of the dielectric constant is known. They can be quantitatively understood if the two influences are referred back to measurable quantities which can be related to the molecular structure.

The polarizability α , in the case of molecules without dipoles, can be brought into a simple relationship with the dielectric constant ϵ , namely

$$\frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{M}{d} = \frac{4\pi}{3} N\alpha.$$

In this equation for *molecular polarization*, M represents the molecular weight, d the density and N the LOSCHMIDT number. In the case of gases, for which ϵ is nearly equal to 1, $\frac{\epsilon - 1}{\epsilon + 2}$ can be replaced by $\frac{\epsilon - 1}{3}$, so that the polarizability becomes

$$\alpha = (\epsilon - 1) \frac{M}{4\pi Nd}.$$

The *dipole moment* μ serves as a measure of the dissymmetry of the charge distribution, and is defined as the product of charge and distance:

$$\mu = e.a.$$

In its derivation, one thinks of all the positive and all the negative charges in the molecule as combined in their centres of gravity, and works with the distance a between these two centres. The order of magnitude of the dipole moment follows from this: e is of the order of magnitude of the elementary unit of charge, 4.80×10^{-10} e.s.u. and a of the order of magnitude of the atomic distances within molecules, 10^{-8} cm, giving together 4.8×10^{-18} e.s.u. cm. Thus μ obtains the order of magnitude of 10^{-18} e.s.u. cm, frequently known as one *Debye* and abbreviated to D⁶⁸.

The polarizability of dipolar molecules cannot be simply derived from the dielectric constant on account of the orientation effect. In order to avoid the orientation effect, a measurement of their dielectric behaviour can be

⁶⁸ Derivation by P. DEBYE, *Polare Molekeln* (Leipzig, 1929). Cf. W. HÜCKEL, *Theoretische Grundlagen der organischen Chemie* II, p. 43 ff (5th Ed., 1948).

undertaken in an alternating electric field whose frequency is so high that the sluggish molecules are unable to keep pace with it. Such fields polarize only intramolecularly. A result of this polarization by an alternating field is a propagation of the electromagnetic vibrations in the dielectric with a velocity which is diminished relative to a vacuum, in consequence of which a refraction occurs which is measured by the refractive index n , this being simply related to the dielectric constant by

$$\epsilon = n^2.$$

Since the relation holds for substances having dipoles as well as those without, and since one has in visible light conveniently accessible alternating fields of high frequency, the expression which is usually employed for calculating the polarizability is

$$\frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d}, \text{ the molecular refraction.}$$

For gases ($n \approx 1$), this is to be simplified to $(n - 1) \frac{M}{3d}$. The relationship $\epsilon = n^2$ is valid in the limiting case for very long wave-lengths, for which the covibration of the electrons can be neglected.

Dipole moments of gaseous substances. — Although in principle the dielectric constant of a gas thus enables the polarizability to be determined, it is almost never used for this purpose on account of the much simpler measurement of the refractive index. On the contrary, by determining the temperature-dependence for dipolar molecules, the temperature-independent polarizability α is eliminated from the equation which in addition to α also contains the dipole moment μ , in order to calculate the latter:

$$(\epsilon - 1) \frac{M}{d} = 4\pi N\alpha + \frac{4\pi\mu^2}{kT}.$$

$$\left(k = \frac{N}{R} = \text{the BOLTZMANN constant} = 1.371 \times 10^{-16} \text{ erg per degree}\right).$$

Dipole moments of dissolved substances⁶⁹. — One thus makes use of the dielectric constant in order to derive the dipole moment from it. The formula given here for its calculation is valid only for gases. But it is also possible to calculate dipole moments from the dielectric constants of solutions which contain polar molecules dissolved in a large excess of dipole-free liquid. Here the temperature-dependence of the dielectric constant is not required. Instead, the molecular polarization of the solution is calculated from the dielectric constant, and that of the dissolved substance obtained by subtraction of the molecular polarization of the pure

⁶⁹ For further, see P. DEBYE, *Polare Molekeln*; W. HÜCKEL, *Theoretische Grundlagen der organischen Chemie* II, p. 50 ff (5th Ed., 1948).

solvent. The temperature-independent fraction for distortion, also briefly known as the displacement polarization, must also be subtracted in order to obtain the influence of the dipole on its own. This *distortion polarization* is composed of two parts, the one being due to the displacement of electrons in an electric field — electron polarization P_E — and the other to the displacement of the nuclei in an electric field — atom polarization P_A . The first fraction can, with sufficient approximation, be put equal to the molecular refraction observed in the visible region. For the *atom polarization*, which is always appreciably smaller, 5—10 % of the electron polarization, can usually be inserted with sufficient precision, and under certain circumstances can also be evaluated indirectly. Taking the distortion polarization into account, the dipole moment is obtained from the total polarization P at the temperature T by the equation

$$\mu = 0.01273[P - (P_E + P_A)]T \times 10^{-18} \text{ e.s.u. cm.}$$

Quite a different method of measuring dipole moments depends on the deflection of molecular beams in an inhomogeneous electric field⁷⁰. The broadening of the beam is determined by the magnitude of the dipole moment. The precision of the method is not high, which is why it has only been applied in rare cases, as in the determination of the dipole moments of the gaseous alkali halides (Chapter VIII, 7, (iv)). Consequently, brief reference to it will suffice here.

(ii) Dipole Moment and Constitution

Since the dipole moment provides no details about the distribution of charges, but makes only summary pronouncements concerning the positions of their centres of gravity, it is able to contribute only to a relatively modest extent towards a knowledge of the state of bonding. In combination with other observations, however, it provides valuable indications and criteria. That the hydrogen chloride molecule possesses a dipole moment — 1.04 D — is not surprising. If the experimental value for the moment is combined with the internuclear H—Cl distance, 1.28 Å, determined in other ways (from the infra-red spectrum), it is seen that not even an approximately heteropolar compound with the centre of gravity of negative charge in the chloride ion is under examination, since the moment would then have to be $4.80 \times 1.28 \times 10^{-18} = 6.1 \text{ D}$ (p. 68). From the fact that water has a dipole moment — 1.84 D — follows only its unsymmetrical structure. Whether this dissymmetry is ascribable to a bent structure or to dissimilar distances of the hydrogen atoms from the oxygen in a linear molecule, must be decided by special measurements — rotation spectrum⁷¹ — or by theoret-

⁷⁰ H. KALLMANN and F. REICHE, *Z. Physik*, 1921, 6, 352; O. STERN and E. WREDE, *ibid.*, 1927, 44, 261.

⁷¹ H. RUBENS, *Sitzungsber. preuss. Akad. Wiss. Berlin*, 1913, p. 513; H. RUBENS and G. HETTNER, *ibid.*, 1916, p. 167; R. MECKE, *Z. Physik*, 1933, 81, 313.

ical considerations ⁷². These have resulted in a bent structure, $\text{H} \begin{array}{c} \diagup \\ \text{O} \\ \diagdown \end{array} \text{H}$,

and *not* $\text{H}-\text{O}-\text{H}$. The same holds for other triatomic molecules like H_2S ($\mu = 0.93$ D) and SO_2 ($\mu = 1.6$ D ⁷³), which are likewise angular. By way of contrast, carbon dioxide, which has no dipole moment, must be linear ⁷⁴. Dipole moments are also absent in the mercuric halides HgCl_2 , HgBr_2 and HgI_2 , which are likewise linear. If, for bent molecules, the angle and atomic distances are known, it is possible to state the polarity of the individual bonds. Without such knowledge, this is not possible. Thus, for example, the dipole moment decreases considerably in the series NH_3 , PH_3 , AsH_3 . The reason for this may be either a flattening of the pyramid at whose apex the element linked to the hydrogen is situated, or a decrease in the polarity of the X—H bonds. Only the ascertainment — made with the help of the infra-red spectrum and diffraction of electrons — that the pyramid angles in these compounds are almost the same at about 100° makes it possible to decide that the reduction in dipole moment rests on a decrease in polarity of the X—H bonds ⁷⁵ (pp. 359, 412). Admittedly, yet a third possibility must be brought into consideration, namely that the lone electron pairs in $:\text{NH}_3$, $:\text{PH}_3$ and $:\text{AsH}_3$ participate to different extents in the setting up

of a dipole moment in the sense of the formulae $\leftarrow \begin{array}{c} \text{---} \text{H} \\ \text{---} \text{N} \text{---} \text{H} \\ \text{---} \text{H} \end{array}$, strongly

displaced outwards from the apex of the pyramid, and $\leftarrow \begin{array}{c} \text{---} \text{H} \\ \text{---} \text{As} \text{---} \text{H} \\ \text{---} \text{H} \end{array}$, weakly

displaced outwards from the apex of the pyramid. Molecules of the formula XY_4 , e.g., CCl_4 , SiF_4 and $\text{Ni}(\text{CO})_4$, as far as is yet known ⁷⁵, always have a zero dipole moment. They thus have either a three-dimensional tetrahedral or a planar square structure. Again, measurements of another kind must decide between the two possibilities.

The CO and NO molecules, which without question are unsymmetrical, have moments lying at the limit of measurability, namely about 0.15 D. The difference in nuclear charge of the two different atoms must hence be almost

⁷² W. HEISENBERG, *Z. Physik*, 1924, **26**, 196; F. HUND, *ibid.*, 1925, **31**, 81; **32**, 1.

⁷³ For SO_2 the bent structure also follows from the negative KERR constant (cf. p. 352).

⁷⁴ H. A. STUART, *Z. Physik*, 1928, **47**, 457.

⁷⁵ On p. 71 of H. J. EMELÉUS and J. S. ANDERSON's *Modern Aspects of Inorganic Chemistry* (Routledge, London, 1938), a flattening of the pyramid is erroneously assumed to be the cause without a discussion of the two possibilities.

⁷⁶ It appears completely within the bounds of possibility that the tetrahalides of groups V and VI, e.g., VCl_4 , SF_4 , SeF_4 , TeCl_4 and TeBr_4 , possess dipole moments in consequence of a pyramidal structure. For TeCl_4 dissolved in benzene, a considerable moment (2.57 D) has been found: K. A. JENSEN, *Z. anorg. Chem.*, 1943, **250**, 247. Cf. Chapter VI, p. 416. According to the most recent electron-diffraction measurements, VCl_4 is regularly tetrahedral (Chapter VII, 3, (iii)).

compensated — or alternatively slightly overcompensated — by a corresponding structure of the electron cloud. In any case, these molecules cannot contain semi-polar bonds (p. 93). Whether here the oxygen or respectively the carbon or nitrogen forms the negative end of the weak dipole, remains undecided by the dipole measurements.

For the molecule of carbon oxysulphide OCS, for which in analogy to CO_2 and CS_2 a linear structure is to be presumed⁷⁷, a moment is to be expected on account of the dissymmetry. This has been found to be 0.65 D. Its direction can be given by way of conjecture when the magnitudes of the moments of organic compounds containing the $\text{C}=\text{O}$ and $\text{C}=\text{S}$ groupings are referred to for comparison. Since the thioaldehydes and thio-ketones have larger moments than the aldehydes and ketones, it may be assumed that in carbon oxysulphide the centre of gravity of the negative charges lies over towards the sulphur. This conclusion is however not binding, since the state of bonding predominating between the atoms is not the same as in organic compounds, there being namely in carbon oxysulphide a strong mutual influencing of the bonds which proceed from the same carbon atom to O and S, and which are usually written as double bonds, $\text{O}=\text{C}=\text{S}$. Certainly, it is not exactly probable, in consequence of this interaction between the bonds in carbon oxysulphide, that the difference in polarity otherwise observed between the $\text{C}=\text{O}$ and $\text{C}=\text{S}$ bonds should be reversed. With certain reservations, it can further be concluded from these polarities that the OCS molecule is not a simple dipole, but one with two negative

ends comprised of two individual dipoles, namely $\text{O}=\overset{+}{\text{C}}=\overset{-}{\text{S}}$. (The stronger shifting of the negative sign towards the S symbol is to signify that the electrons are presumably more strongly displaced towards the sulphur than towards the oxygen.) In the symmetrical carbon dioxide and carbon disulphide molecules, the bonds between C and O and likewise C and S are certainly also polar. But, since they are identical, they neutralize each other in their effects, so-called linear quadrupoles, $\overset{-}{\text{O}}=\overset{+}{\text{C}}=\overset{-}{\text{O}}$ and $\overset{-}{\text{S}}=\overset{+}{\text{C}}=\overset{-}{\text{S}}$, being present.

Regarding the electron distribution in the bonds themselves and the state of bonding between the carbon and oxygen or sulphur, nothing can be gathered from the moment of carbon oxysulphide, or from the absence of moments for the dioxide and disulphide.

In nitrogen dioxide NO_2 , in analogy to other compounds containing an $\text{N}=\text{O}$ bond, a fairly considerable polarity will likewise have to be assumed

⁷⁷ This linear structure also follows from the molecular heat determined by ultrasonic measurements: A. EUCKEN and S. AYBER, *Z. physik. Chem.*, 1940, B 46, 195; A. EUCKEN and K. SCHÄFER, *ibid.*, 1941, B 51, 60. On the other hand, the interpretation of the depolarization factor of a RAMAN line by J. WAGNER, *ibid.*, 1941, B 48, 309, according to which interpretation the molecule should be bent, possesses no conclusiveness.

for the individual bonds, even if again here a strong mutual influencing takes place. But since the moment of NO_2 is only 0.4 D, its molecule must be either very slightly bent or, if straight, contain not quite equally bonded oxygen atoms. On association to N_2O_4 the moment becomes smaller, perhaps even totally disappearing.

Whereas very special symmetries must be assumed when a dipole moment is lacking, namely such that contain a centre of symmetry, the existence of a moment usually allows of several possibilities, as has been discussed in the cases of water and nitrogen dioxide. As an example of a molecule consisting of more than three atoms, that of hydrogen peroxide might be cited, since for this various structural formulae have formerly been considered. It provides a good example of the conclusions concerning the structure which can be drawn from the dipole moment, and how certain these are ⁷⁸.

Hydrogen peroxide has a moment of about 2.1 D, the data varying between 2.06 and 2.13. It may thus not possess the symmetrical structures

$\text{H}-\text{O}-\text{O}-\text{H}$ or $\begin{array}{c} \text{H} \\ \diagup \\ \text{O}-\text{O} \\ \diagdown \\ \text{H} \end{array}$. It must appear questionable whether it is

at all possible to assign to the molecule an unchangeable spatial arrangement with definite positions for the hydrogen atoms, since, as in the case of the single C—C bond, a rotation of the substituents situated on the oxygen is possible in consequence of free rotation (cf. p. 377 ff). In hydrogen peroxide such a rotation will be more complete than for ethane, since, with the latter, the three H atoms of each CH_3 group must be rotated past one another, which, as a result of their interaction, demands a certain expenditure of work. For hydrogen peroxide, on the other hand, in rotating about the O—O axis the two hydrogen atoms need not pass one another. It can therefore be assumed that all the possible positions will be approximately equally abundant, and that the measured dipole moment will be a mean value of the moments for all possible models (including the centrosymmetrical). This mean value could be calculated from the model if the $\text{O}-\text{O}-\text{H}$ angle and

the moment of the O—H bond were known. These values cannot be obtained from dipole measurements alone. However, if they are assumed to be the same as for water, they can then be derived from the model of the water molecule and its dipole moment. With an angle of 105° at the oxygen and a total moment of 1.84 D, the resulting individual moment of an O—H bond is 1.58 D. On inserting these figures under the assumption that all the possible positions for the hydrogen atoms are equally abundant, the dipole moment 2.10 D is calculated for hydrogen peroxide, in agreement with observation. Even though this agreement may be coincidental, since the suppositions underlying the calculation are not absolutely certain, such an eventuality is nevertheless very improbable. The formula $\text{HO}-\text{OH}$ will

⁷⁸ W. THEILACKER, *Z. physik. Chem.*, 1933, **B 20**, 142.

therefore be preferred to the unsymmetrical formula $\begin{matrix} \text{H} \\ \text{H} \end{matrix} \text{O}=\text{O}$ often considered previously, which formula would also require a considerable dipole moment. Admittedly, a certain proof is only to be obtained from the RAMAN spectrum of hydrogen peroxide ⁷⁹.

Considerations of the kind which have here been depicted for the instances of a few compounds can only rarely be applied with any reliability to inorganic compounds on account of the considerable mutual influencing of the bonds in small molecules. On the other hand, they are of much greater significance in organic chemistry, in which the individual parts of the larger molecules and also their bonds may be regarded as to a fair extent independent of one another. For this reason, dipole moments have attained a much greater importance for the investigation of constitution in organic chemistry than they have in inorganic chemistry. It is to be regretted that it is not possible to determine the dipole moments of ions in solution or in crystals, and thus obtain information concerning their polarity, *e.g.*, that for ClO' , and their spatial structure. For this, other methods are necessary — X-ray analysis and infra-red spectroscopy — in order, for example, to ascertain that the CO_3'' and NO_3' ions are planar and the ClO_3' and BrO_3' ions pyramidal.

It remains finally to point out with a few examples that liquids consisting of dipolar molecules certainly possess in general higher dielectric constants than those consisting of molecules without dipoles, but that no simple relationship exists between the size of the moment of the molecule of a gas and the dielectric constant of the substance in the liquid state. In this connection, the following brief table is given ($t = 20^\circ\text{C}$):

	μ	ϵ	$\mu = 0$	ϵ
H_2O	1.84 D	81	CCl_4	2.25
H_2O_2	2.1	94	C_6H_6	2.25
HCl	1.08	4.6	CS_2	2.61
HBr	0.78	3.8	SiCl_4	2.4
CH_3OH	1.65	31	SnCl_4	3.2
$(\text{C}_2\text{H}_5)_2\text{O}$	1.18	4.63		
HCN	3.03	114.9 ⁸⁰		
CH_3CN	3.44	36.4		
$\text{C}_6\text{H}_5\text{NO}_2$	4.24	34.0		

(iii) Refraction of Light

The refraction of visible and ultra-violet light enables pronouncements to be made concerning the type of bonding between the atoms, since it is

⁷⁹ A. SIMON and F. FEHÉR, *Z. Elektrochem.*, 1935, **41**, 290; F. FEHÉR, *ibid.*, 1937, **43**, 663. Cf. p. 377.

⁸⁰ 191.9 at -10° , 158.1 at 0° , 133.3 at $+10^\circ$: G. E. COATES and J. E. COATES, *J. Chem. Soc.*, 1944, p. 77.

governed by an interaction between the electromagnetic waves of the radiation traversing the refractive medium and the most loosely bound electrons, the valence electrons. This interaction causes light to be propagated more slowly in any medium than in empty space, in consequence of which light is always refracted towards the perpendicular according to the SNELLIUS law: refractive index $n = \frac{\sin \alpha}{\sin \beta}$. The refractive index increases with decreasing wave-length of the light as long as one remains reasonably far removed from the region of absorption. This phenomenon is known as *dispersion*. If the frequencies of the light and electrons agree, a strong absorption of the radiation is observed which may to a certain extent be compared with the phenomenon of resonance between two oscillatory systems. In the proximity of the absorption regions, anomalous dispersions occur. Further away a dispersion formula can be set down and theoretically established, this reproducing the connection between the refractive index for a particular wave-length and the characteristic frequencies of the electrons. For our purpose, we will not solve it for n^{81} , but formulate it so that the *polarizability* a_ω appears as a factor in it. This polarizability is distinguished from the polarizability measured in a stationary field by the subscript ω , which signifies the frequency of the exciting vibration. From the classical theory of dispersion⁸², which works with quasi-elastically bound electrons of characteristic frequencies ω as the oscillatory structures in the atom or molecule, the formula that is obtained is as follows⁸³:

$$\frac{n_\omega^2 - 1}{n_\omega^2 + 2} \cdot \frac{M}{d} = \frac{4\pi}{3} N a_\omega = \frac{4\pi}{3} N \frac{e^2}{m} \sum \frac{1}{\omega_i^2 - \omega^2}$$

(where M is the molecular weight, d the density, N the LOSCHMIDT number, e the charge and m the mass of an electron).

The *molecular refraction* or, more briefly, *mol refraction*, related here to the characteristic frequencies of the electrons, is, since it is proportional to the polarizability, a measure of the latter.

As is seen, a factor is included in the molecular refraction which contains the sum of the actions of all the oscillatory electrons. It is thus, just as is the polarizability, a "bulk effect" which combines the effects of the various individual bonding electrons within itself in a none too extricable manner. A simple evaluation would be possible only if all the bonding electrons possessed the same frequencies, and, under this only very conditionally valid supposition, it is also possible in the case of suitable substances to

⁸¹ As in the CAUCHY equation $n - 1 = A \left(1 + \frac{B}{\lambda^2} \right)$.

⁸² We need not concern ourselves here with the formula for the quantum-mechanical theory of dispersion, which is very similar in appearance.

⁸³ Derivation in, e.g., W. HÜCKEL's *Theoretische Grundlagen der organischen Chemie*, Vol. II, p. 104 ff (5th Ed., 1948).

calculate approximately the number of bonds from the dispersion formula. Conversely, however, since in general the bonding electrons do not by any means all have the same frequencies — except perhaps in the H_2 molecule — it is not possible to calculate the characteristic electron frequencies from the dispersion. Only this much may be qualitatively asserted, namely that a relatively high molecular refraction is to be attributed to the presence of electrons of low frequencies which are bound more loosely than usual. Thus, for example, if one compares the molecular refractions of the two isomeric C_6H_{12} hydrocarbons cyclohexane and hexene, and finds that that for hexene is appreciably the greater, this fact may be explained by the particularly loosely bound electrons which hexene contains in its double bond. With regard to the number of these and their frequencies, the molecular refraction tells one nothing. Quite generally, one cannot proceed beyond the assertion that a high molecular refraction and hence large polarizability corresponds to loosely bound electrons of relatively low characteristic frequencies.

The significance of the molecular refraction for investigating the states of bonding also lies in another direction. Namely for organic compounds it is seen to be an approximately additive property upon which the constitutive peculiarities are superimposed. Among the latter, special states of bonding, like double and triple bonds, conjugated double bonds and bonds to oxygen in hydroxyl or ether groups, are to be recognized. Constitutive peculiarities of this type always stand out clearly in an additive scheme when the property is composed in first approximation of terms which are constant and independent of each other. This is the case for organic molecules in which the individual bonds may be regarded as largely independent of one another (cf. p. 90). For small inorganic molecules, however, this prerequisite is hardly ever realized. In inorganic chemistry, therefore, the molecular refraction does not possess anything like the significance for gaining an understanding of the bonding that it does in organic chemistry.

Only where there are approximately equal, slightly influenced bonds is a resolution of the molecular refraction into additive terms like atomic refractions — one might also work with bond refractions — also found to be feasible for inorganic compounds. Conversely, where such a possibility of resolution exists, it proves the approximate similarity of the compared bonds.

Thus the atomic refractions of hydrogen, chlorine and bromine, which are obtained by halving the molecular refractions found for the H_2 , Cl_2 and Br_2 molecules, are closely equal to the values for the atomic refractions of H, Cl and Br which are derived from organic compounds containing the elements linked to carbon. From this it may be concluded that the bonding in the H—H and C—H, Cl—Cl and C—Cl, and Br—Br and C—Br bonds must be really similar. Likewise the molecular refractions of HCl and HBr agree approximately with the sums of the atomic refractions of H with Cl and Br respectively (cf., in this connection, p. 411).

(iv) KERR Effect

A combination of dielectric action and the refraction of light is observed in the KERR effect⁸⁴. With this is understood the phenomenon in which a normally isotropic medium becomes doubly refracting in an electric field. If the refractive index in the field direction is larger than at right angles to it, the effect is positive: otherwise it is negative. Its magnitude is measured by the KERR constant B , in which n_p and n_s , the refractive indices parallel and vertical to the field direction, E , the field strength, and λ_v , the wave-length *in vacuo* of the light employed, are found linked together in the following manner:

$$B = \frac{n_p - n_s}{\lambda_v E^2}$$

Instead of this definition of the KERR constant, another is also used in which, apart from the field strength, only refractive indices appear, wherein, accordingly, the difference between the refractive indices n_v and n_s relative to the refractive index n of the medium when not subjected to a field is considered:

$$K = \frac{n_p - n_s}{n E^2}$$

Since n and the wave-length λ_v measured in a vacuum are connected with the wave-length λ measured in the isotropic medium by the relation $\lambda_v = n\lambda$, K and B are related in the ratio $\frac{K}{B} = \lambda$.

The KERR effect is not observed with all substances. The rare gases do not exhibit it. It must therefore be linked with the molecular structure of the substance. The nature of this relationship appears from the consideration that the molecules become orientated in an electric field, whether on account of polarization alone or on account of polarization plus dipole orientation. If now a molecule is not perfectly spherically symmetrical, in consequence of its different polarizabilities in different directions, it will, depending upon its orientation, influence the propagation of light in distinguishable ways. If, on applying an electric field, an orientation of a large number of molecules occurs, the dielectric must in consequence become birefringent.

Concerning the magnitude of the effect for various substances, the following general statements can be made by way of comparison. The orientation of a molecule in an electric field is determined by the symmetry of its charge distribution and also by the polarizability in different directions. A molecule without a dipole moment but with *anisotropy of polarizability* will try to orientate itself in the field in such a way that the axis of maximum polarizability lies in the direction of the field, because the largest moment

⁸⁴ Detailed presentation: H. A. STUART, *Ergebn. exakt. Naturw.*, 1931, **10**, 159; *Molekülstruktur*, p. 197 (Springer, Berlin, 1934); G. BRIEGLER and K. L. WOLF, *Fortschr. Chem. Physik und physik. Chem.*, 1931, **21**, 1; *Lichtzerstreuung, Kerreffekt und Molekülstruktur* (Bornträger, Berlin).

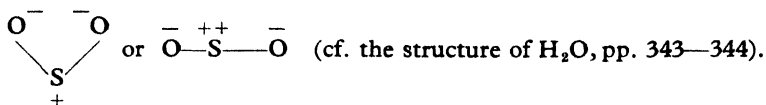
is induced along this axis. Through this orientation, therefore, the polartzability and hence also the interdependent refractive index for substances consisting of such molecules will become greater in the field direction than perpendicular to it, that is, the KERR constant becomes *positive*.

For non-polar molecules, only the induced moment effects an orientation in an electric field; for dipolar molecules, there is an additional permanent moment. In general, the permanent moment and the maximum polarizability will not agree as to direction, but make an angle with one another. Apart from the relatively rare cases in which the dipole moment is very small and the polarizability in one direction unusually large — these will not be considered in what follows — the permanent moment will exceed the induced moment in magnitude, and consequently act as the primary determining factor with regard to the orientation in an electric field. For a detailed treatment, the KERR constant can in the case of dipolar substances be split into two additive terms, an anisotropy term and a dipole term, of which the latter is usually considerably the greater. They can be distinguished by the nature of their temperature-dependence.

There are two characteristic limiting cases for the relative orientation of dipole moment and axis of maximum polarizability, in which either the two directions coincide or are perpendicular to each other. In the former case, the effects reinforce each other; also, on account of the strong orientating action of the moment, the molecules will orientate themselves much more perfectly in the direction of their axis of maximum polarizability than would non-polar molecules, that is, the KERR constant will assume a *large positive* value. If, on the other hand, the moment and axis of maximum polarizability are at right angles to each other, as a result of the strong orientating action of the moment — provided this is not too small — the axis of greatest polarizability will be rotated out of the field direction into that perpendicular to it. In consequence, the refractive index perpendicular to the field direction becomes larger than that in it, that is, the KERR constant is *negative*. Substances whose molecules approach these limiting cases of intramolecular arrangement of moment and axis of maximum polarizability will, with respect to the sign of the KERR constant, still behave like the limiting cases. For angles between the two directions which differ considerably from 0° or 90° , the KERR constant may be positive or negative, according to the magnitude of the dipole moment and according to the magnitude and degree of asymmetry of the polarizability.

Of the few examples from inorganic chemistry in which the KERR effect can be drawn upon for the elucidation of the molecular structure — organic chemistry provides very many more — that of sulphur dioxide will be quoted. For this substance, a bent structure is derived with certainty from the KERR effect. Sulphur dioxide has a fairly large dipole moment of 1.6 D, and its KERR effect is negative. The dipole moment can arise either from a bent molecule in the case of similar bonding of the two oxygen atoms, or, in the

event of a linear structure, from dissimilar linking of the two oxygen atoms to the sulphur atom, either with respect to distance or polarity:



The axis of maximum polarizability in the case of linear molecules always lies in the direction of the molecular axis, for the bonding electrons are to be found between the atoms on this axis and in proximity to it. They are more easily displaced in the direction of this axis or parallel to it than at right angles thereto, whereby they would arrive at positions which they would not normally be able to assume. For the linear SO_2 model, the dipole moment likewise lies in the direction of the molecular axis, that is, if the model were correct, a large positive KERR constant would need to be present. But since, on the contrary, a negative KERR constant is observed, the linear SO_2 model cannot correspond to reality, and the molecule must be bent.

The linear, dipole-free molecule of carbon dioxide has a small positive Kerr constant. It is to be expected of carbon oxysulphide $\text{O}=\text{C}=\text{S}$, which has not yet been investigated with respect to the KERR effect, but which possesses a dipole moment in the direction of the molecular axis and is thus analogously constructed to the incorrect linear SO_2 model, that it possesses an appreciably greater positive KERR constant than carbon dioxide.

By including other properties, namely the mean polarizability of the molecule and the depolarization of the scattered radiation, it is possible, for simple molecules like CO_2 and SO_2 , to calculate the principal polarizabilities in three mutually perpendicular directions. Only in individual cases, however, can such calculations be accomplished, either completely or in part. The degree of depolarization of scattered light, which is employed in this and is likewise connected with the anisotropy of polarizability, has also been applied only rarely to the determination of the molecular structure of inorganic molecules. A discussion of it will therefore be omitted here⁸⁵.

6. Light Absorption and Emission

(i) General

The process of interaction between radiation and matter which leads to light absorption could, in analogy to the excitation of an oscillatory mechanical system by a periodic impulse, be understood as a resonance phenomenon. This analogy is however not so far-reaching that a useful theory of light absorption could be erected upon it. Indeed, even today there is still no such theory which is completely satisfying; rather, one must be satisfied with a presentation which is half quantum-mechanical and half classical. It is also not possible to work simply with certain characteristic frequencies

⁸⁵ Application to organic molecules: W. HÜCKEL, *Theoretische Grundlagen der organischen Chemie*, Vol. II, p. 130 ff (5th Ed., 1948).

of electrons treated like harmonic oscillators, as has been done for the interpretation of dispersion in the classical dispersion theory; for, according to the quantum theory, the electron is not an oscillator capable of a fundamental and several harmonic vibrations, but can, from a ground state, be raised to numerous excited states corresponding to different discrete energy values. The transitions between all these various possible states, for which different transition probabilities exist, are connected with the quantized assumption and liberation of energy in the absorption and emission of spectral lines.

With this state of affairs, it appears in general expedient to proceed from various possible absorption and emission processes in the molecule and find the frequencies to which they correspond. In principle, the process of quantized absorption and emission is the same as for the atom. In the absorption of a vibration of frequency ν or in the emission of a spectral line of the same frequency, the respective assumption or liberation of energy $h\nu$ results, this corresponding to the difference in energy between two possible states of the atom, that is, the difference between two energy terms. For the molecule, the position is complicated relative to the atom, in that the motion of the nuclei must also be taken into consideration. The nuclei can rotate about the centre of gravity of the system, and carry out vibrations in addition. In consequence of this, a *rotation spectrum* and a *rotation-vibration spectrum* exist for molecules. (A vibration spectrum alone cannot occur since, whereas a rotation without simultaneous vibration of the nuclei can be realized, a nuclear vibration without simultaneous rotation cannot.) This vibrational excitation among molecules is additional to the excitation of the electrons. All these vibrations influence one another reciprocally. However, this influencing is in general small, since the individual frequency processes correspond to frequencies which are usually well-separated, so that each kind of vibration falls in a spectral region of its own and resonance between them does not occur. Consequently, generally with good approximation, the vibrational energy can be represented in the following manner as the difference of two energy terms with neglect of the interaction between nuclear vibration and rotation as well as of that between electronic and nuclear motion:

$$\begin{aligned} h\nu &= (E_e + E_v + E_r)_1 - (E_e + E_v + E_r)_2 \\ &= (E_{e_1} - E_{e_2}) + (E_{v_1} - E_{v_2}) + (E_{r_1} - E_{r_2}). \end{aligned}$$

E_e here signifies the energy terms for electronic transitions, and E_v and E_r those for nuclear vibration and rotation.

The differences between the electronic terms, which do not concern us immediately here, correspond to frequencies which lie in the visible and ultra-violet part of the spectrum ($> 10^4 \text{ cm}^{-1}$); the differences between the vibrational-energy terms lie in the infra-red (100 to 1000 cm^{-1}) and those between the rotational levels in the far infra-red ($< 100 \text{ cm}^{-1}$). There are thus three spectral regions from which it is individually possible to learn something concerning:

- | | | | |
|--|-------|------|-------------|
| (i) electronic transitions in the wave-length region | 0.15— | 0.8 | μ ; |
| (ii) nuclear vibrations | „ „ „ | 1 — | 10 μ ; |
| (iii) rotation of the nuclei | „ „ „ | 50 — | 500 μ . |

Since the electronic transitions are influenced by the term differences $E_{v_1} - E_{v_2}$ and $E_{r_1} - E_{r_2}$, they do not result in single spectral lines, but, as a consequence of the large number of term differences with a modifying influence, in a large number of closely adjacent lines. In the electronic band spectrum, therefore, in the place of *one* line corresponding to the term difference $E_{e_1} - E_{e_2}$ is found a multiplicity of lines arising by the simultaneous change of all the quantum numbers which come to be considered for the differences $E_{v_1} - E_{v_2}$ and $E_{r_1} - E_{r_2}$.

An electronic band spectrum of this type can now be subjected to an analysis, in which, for each line of frequency ν , the energy difference $h\nu$ is calculated and the term evaluated from the latter. The rotational structure, that is, the multiplicity of each vibrational process caused by the rotation, is analyzed first. Such analyses are very complicated, and usually only possible in the case of diatomic molecules. Although in principle one can learn everything from such concerning the possible electronic states, they nevertheless tell the chemist little as long as he is unaware which of the states thus described are of significance for chemical reactions, and what changes they undergo thereby.

Without analyzing the electronic band spectrum in detail, it can be employed for the evaluation of a quantity which is very important thermodynamically, namely the *heat of dissociation* or *dissociation energy*. For this, a knowledge is required of the limit towards shorter wave-lengths at which the band spectrum, which consists of lines, passes over to a continuous spectrum. This transition indicates that, on the appearance of a vibration with a particular frequency ν_D , a well-defined, energy-rich state of the molecule no longer occurs by absorption, but that dissociation sets in. The energy $h\nu_D$ then corresponds to the energy of dissociation for the dissociation process effected by radiation. This is not necessarily identical with thermal dissociation, for, when energy of radiation remains with the products of dissociation, at least one excited dissociation product is formed, in the simplest case of a diatomic molecule, one excited atom together with one unexcited atom. The heat of dissociation calculated from the energy of the radiation is then larger than the thermal value, and that by the amount of energy which distinguishes the state of the excited atom from its ground state. If this *excitation energy* can be calculated by other means, then the heat of dissociation for thermal decomposition can be calculated from the dissociation energy found with the aid of light radiation⁸⁶.

⁸⁶ This reasoning was first developed by J. FRANCK (*Trans. Faraday Soc.*, 1925, 21, 536) for the iodine molecule. The convergence limit given subsequently is more precise than that employed by FRANCK.

A calculation of this kind can be accomplished very exactly for the instance of the iodine molecule. The transition of the bands into a continuous spectrum here lies in the visible at 4989.3 Å, and can be determined very exactly⁸⁷. This wave-length corresponds to an energy $h\nu = 2.484 e\text{-volt}$ (1 $e\text{-volt}$ = electron volt = the kinetic energy which an electron obtains on passing through a potential drop of 1 volt, being numerically equal to 2.3053×10^4 cal/mol). One iodine atom in the ground state is formed, together with one excited atom. For the iodine atom, the energies of its excited states can be derived from its electron-shell structure. The two states lying nearest to the ground state are richer in energy by 0.942 and 6.9 $e\text{-volt}$. Since the energy of the exciting radiation amounts to only 2.484 $e\text{-volt}$, it cannot possibly lead to an iodine atom at a level 6.9 $e\text{-volt}$ higher than the ground state. Consequently only the state excited to the extent of 0.942 $e\text{-volt}$ comes into consideration, the thermal heat of dissociation being smaller than 2.484 $e\text{-volt}$ by this excitation energy, that is, it corresponds to $1.542 \pm 0.001 e\text{-volt}$ or 35.55 kcal per mol. That indeed iodine atoms are formed on irradiating iodine with light of wave-length 4989.3 Å has been proved by various experiments⁸⁸.

For the hydrogen molecule, a completely corresponding calculation can be carried out. This has provided a thermal heat of dissociation of 103.20 ± 0.02 kcal from the frequency $118,376 \text{ cm}^{-1}$ at the transition to the continuous spectrum⁸⁹. The energy of the radiation which effects decomposition into one ground-state and one excited hydrogen atom is here greater by the excitation energy 235.06 kcal, that is, equal to 338.26 kcal or 14.673 $e\text{-volt}$.

Frequently the calculation of dissociation energies is much less certain than in the case of the examples quoted here⁹⁰. This is usually⁹¹ due to the fact that the point of convergence of the individual lines to the continuous spectrum cannot be exactly determined experimentally, as when in the neighbourhood of this position the vibrational levels, which correspond to individual lines, are too closely heaped together. Often, also, the line spectrum breaks off prematurely. In order, nevertheless, to be able to calculate at least approximately in these cases such a thermally important quantity as the dissociation energy from the spectrum, the point of convergence of the vibrational levels, at which with regular continuation of the sequence the continuous spectrum would begin, must be found by *extrapolation* of the

⁸⁷ W. G. BROWN, *Phys. Rev.*, 1931, [ii], **38**, 709.

⁸⁸ E. G. DYMOND, *Z. Physik*, 1925, **34**, 553; K. F. BONHOEFFER and L. FARKAS, *Z. physik. Chem.*, 1928, **A 132**, 235; H. SENFTLEBEN and E. GERMER, *Ann. Physik.*, 1929, [v], **2**, 847; L. A. TURNER, *Phys. Rev.*, 1928, [ii], **31**, 983.

⁸⁹ H. BEUTLER, *Z. physik. Chem.*, 1935, **B 29**, 315.

⁹⁰ Cf., for example, the discussion concerning the determination of the dissociation energy of carbon monoxide from the photodissociation: A. G. GAYDON and W. G. PENNEY, *Nature*, 1942, **150**, 406; G. HERZBERG, *J. Chem. Phys.*, 1942, **10**, 306; R. F. SCHMID and L. GERÖ, *Proc. Phys. Soc.*, 1946, **58**, 701.

⁹¹ An uncertainty concerning the excited state in which an atom arising through dissociation is found can also affect the reliability of the estimate.

observable series of lines⁹². The certainty of such extrapolations varies from case to case, and can be estimated from the extrapolation procedure.

Mention must also be made of the fact that there are also other possibilities of deriving the dissociation energy from the molecular spectrum⁹³.

(ii) Infra-red Spectra

Absorption in the infra-red is governed by the rotation of the nuclei and their vibrations relative to each other, the frequencies corresponding to those of infra-red light. Excitation by their electromagnetic vibrations of the latter occurs, but not directly as in the case of electrons, since an interaction between them and oscillating mechanical masses is plainly not possible. Only in so far as the masses behave like systems of electrical charge are they able to participate in an interaction of this kind. Therefore only those material movements respond to infra-red vibrations which generate a periodically changing electromagnetic field with which the incident radiation can interact. The remaining vibrations are inactive.

Rotation-vibration and rotation spectra. — The pure rotation spectrum is produced by a molecule rotating as a rigid structure, in which the position of the nuclei relative to each other has thus to be regarded as fixed. The rotation of a rigid molecule of this type thus generates a field only when it represents a dipole. Molecules without dipoles like H₂, O₂, N₂, CH₄ and CCl₄ do *not* give a rotation spectrum, although they of course also rotate, and are *not* able to absorb any rotational energy from radiation falling on them. In the case of dipolar molecules like HCl, H₂O and NH₃, this is possible, in which case the absorption of energy succeeds by way of quanta. In this, the molecule can assume the various states with discrete values of rotational energy which are possible according to the quantum theory. These energy values can be related to the frequency of the absorbed radiation by a relation which includes the various quantum numbers and the moment of inertia *I* of the molecule with respect to the axis about which it rotates. Under consideration of the selection rule (not to be proved here), according to which a time-dependent dipole moment occurs only with changes of the rotational energy by amounts corresponding to a quantum jump of 1, the following equation holds for the wave number $\tilde{\nu}$ (= number of light waves per cm⁹⁴):

$$\tilde{\nu} = \frac{h}{4\pi^2 c I} (m'' + 1),$$

where *m''* is the quantum number of the term of lowest energy, and assumes the values 0, 1, 2, 3, . . . The rotation spectrum thus supplies the moment

⁹² A much used extrapolation procedure is due to R. T. BIRGE and H. SPONER, *Phys. Rev.*, 1926, [ii], 28, 259.

⁹³ Concerning this, see A. EUCKEN's *Lehrbuch der chemischen Physik* I, p. 488 ff, under γ and δ (2nd Ed., 1938).

⁹⁴ The dimension in cm⁻¹. Often, especially in the case of infra-red and RAMAN spectra, this is incorrectly termed the frequency. The frequency $\nu = c.\tilde{\nu}$.

of inertia. The moments of inertia of simple molecules have the order of magnitude 10^{-40} g cm². In the most general case, when the molecule can rotate about three different principal axes of inertia and possesses three principal moments of inertia I_1 , I_2 and I_3 differing from one another, an equation of this type is valid for each principal moment of inertia, so that, to a certain extent, three rotation spectra are superimposed upon one another:

$$\tilde{\nu}_1 = \frac{h}{4\pi^2 c I_1} (m'' + 1); \quad \tilde{\nu}_2 = \frac{h}{4\pi^2 c I_2} (m'' + 1); \quad \tilde{\nu}_3 = \frac{h}{4\pi^2 c I_3} (m'' + 1).$$

In addition to the rotations about the three principal axes of inertia, yet other rotations occur, so that essentially still more lines occur than correspond to the three principal moments of inertia; for the rotational motion of the molecule is that of an asymmetrical top in which, during rotation about an axis which is not a principal axis of inertia, the position of this axis continually changes. Because of this, the components of the total angular momentum in the direction of the three principal axes of inertia change with time, and the rotation not taking place about the said axis is consequently not resolvable into rotational processes about this axis. Since the quantized vibrational energies which determine the frequencies depend upon these changeable components, no simpler expression can be given for them and the analysis of such a rotation spectrum becomes very difficult.

The state of affairs is simpler for a molecule in which two of the principal moments of inertia are identical, and which is therefore to be treated as a symmetrical top. Here, namely, for each component the angular momentum can be considered as composed of one component in the direction of a specially chosen third principal axis of inertia and one component in a direction perpendicular thereto. In consequence, the rotational motion which takes place when the top is set in rotation about any desired axis can be described by a rotation about the axis of symmetry with a precession of this axis about the axis of angular momentum superimposed. As a result, the expression for the oscillatory energy of rotation is quite simple. Its quantization likewise leads to a simple formula containing the quantum numbers and the two moments of inertia.

In principle, the position of the lines in the rotation spectrum is in each case given by the moment of inertia of the molecule. This can be deduced from the spectrum by a more or less difficult analysis, which in the case of unsymmetrical polyatomic molecules admittedly appears hopeless.

The calculation of the moment of inertia for diatomic dipolar molecules like HCl is simple. The three principal axes of inertia are here at right angles to one another. One of them lies in the direction of the line joining the nuclei. The others can be placed as desired at right angles in a plane perpendicular to the first axis. For the rotation spectrum, a rotation of the dipole about its axis, in which the nuclei retain their positions, is unimportant, since this produces no alternating electric field. On account of the equality of all the directions at right angles to the dipolar axis, it is immaterial for the

absorption about which of them the rotation takes place. Thus the moment of inertia characteristic for this is given directly according to the fore-mentioned formula.

If the dipolar molecule is a symmetrical top whose axis of symmetry coincides with the dipolar axis as in the case of the pyramidally constructed NH_3 , then, of the principal moments of inertia, only that can be calculated for which the direction of the axis is perpendicular to the axis of symmetry; for the rotation of the ammonia molecule about its three-fold axis of symmetry does not give a periodically changing electric field, and is thus also unable to make its presence apparent in the infra-red absorption spectrum.

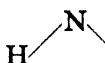
For dipoles which, like the water molecule H_2O , are asymmetrical tops, only in special cases, as precisely in the case of water vapour⁹⁵, has a complete analysis of the rotation spectrum leading to the evaluation of the three principal moments of inertia been accomplished. Here the state of affairs is still to some extent clear, since some series of lines can be recognized in the spectrum by their intensity as belonging together, from which it was possible to estimate the moments of inertia⁹⁶ long before a complete analysis had been accomplished.

(iii) Interatomic Distances from Moments of Inertia

A knowledge of the moment of inertia of a simple molecule enables, since the nuclear masses are known, a calculation of the interatomic distances and hence of the structure of the molecule to be made. However, the rotation spectrum alone is not always sufficient for this, since on occasions, as with ammonia, this does not furnish all the moments of inertia required for the calculation. In the case of diatomic molecules, for which the only determinable dimension is the interatomic distance, the moment of inertia derived from the rotation spectrum suffices for this completely. For HCl , the inter-

atomic distance r is calculated from the moment of inertia $I = \frac{m_1 m_2}{m_1 + m_2} \cdot r^2$


and the values $I = 2.61 \times 10^{-40} \text{ g cm}^2$, $m_{\text{H}} = 1.66 \times 10^{-24} \text{ g}$, $m_{\text{Cl}} = 59.10 \times 10^{-24} \text{ g}$ to be equivalent to $\sqrt{1.62 \times 10^{-16}} = 1.28 \times 10^{-8} \text{ cm}$. For a symmetrical top, as, for example, in the case of ammonia, *two* determinations are necessary, namely the height h of the pyramid and the distance a between the H atoms in the equilateral triangle forming the base (or alternatively the

 H-N-H angle). But the rotation spectrum here supplies only *one* moment of inertia from which, naturally, two independent quantities cannot be calculated. Consequently yet a further independent experimental quantity must here be included, and this is supplied by the infra-red spectrum of deuterioammonia ND_3 , from which its moment of inertia may be obtained.

⁹⁵ R. MECKE, *Z. Physik*, 1933, **81**, 313; W. BAUMANN and R. MECKE, *ibid.*, p. 445; K. FREUDENBERG and R. MECKE, *ibid.*, p. 465.

⁹⁶ A. EUCKEN, *Jahrb. der Radioaktivität und Elektronik*, 1920, **16**, 361.

The two moments of inertia, that of NH_3 at 2.78×10^{-40} and that of ND_3 at 5.40×10^{-40} g cm², both of which are valid for a direction perpendicular to the axis of symmetry, can now be utilized for calculating the height h and the basal edge a of the pyramid, provided the assumption may be made that the interatomic distances and apexal angle are not altered on substituting the hydrogen by deuterium. The justification for this assumption follows from the fact that the distances between H and Cl in HCl and D and Cl in DCl have, from the different moments of inertia, been found to be the same⁹⁷. The calculation, which will not be reproduced here, leads

to the values $h = 0.36 \text{ \AA}$, $a = 1.65 \text{ \AA}$ and hence to an H  H angle lying somewhat above 100° .

A comparison of the moments of inertia of molecules with isotopic elements here enables the molecular dimensions to be calculated. Conversely, since molecules with isotopic elements have different moments of inertia for the same structure and consequently exhibit a somewhat different lay-out of lines in the rotation spectrum, this fact may serve to identify the presence of isotopes. In particular, isotopes like ^{13}C and ^{17}O , which on account of their low concentration had escaped observation in the mass spectrograph, were discovered in this way. The significance of the rotation spectrum thus lies not only in the fact that something is learnt from it concerning the moment of inertia and hence the structure of the molecule, but extends also to isotopic research. From it, the nuclear masses are obtained, although, as already emphasized, it is not the nuclei themselves that enter into interaction with the infra-red light, but only the alternating fields caused by their rotation.

In investigations of this type, one does not always observe the rotation spectrum itself, since this lies in the wave-length region $50\text{--}500 \mu$ which, experimentally, is not very easily accessible. Frequently the frequencies of the rotation spectrum are derived from the rotation-vibration spectrum in the region $1\text{--}10 \mu$, in which one analyzes the rotational structure of the vibrational spectrum.

(iv) Rotation-vibration Spectra

The rotation-vibration spectrum comes into existence through the fact that, in the absorption of infra-red light in the wave-length region $1\text{--}10 \mu$, it is never the nuclear vibrations alone which are influenced. Changes in the rotational quantum numbers occur simultaneously on account of the smallness of the rotational quanta $E_r' - E_r''$. The vibrational and rotational energies thus change at one and the same time, and in place of the frequency

⁹⁷ A difference in the mass of the Cl atom also has virtually no effect on the distance. The moment of inertia for H^{35}Cl is about 0.005×10^{-40} units smaller than for H^{37}Cl .

of a nuclear vibration, $\nu = \frac{E_{v'} - E_{v''}}{h}$, a large number of closely adjacent frequencies appear. Thus, in place of the lines corresponding to the change of energy of a particular nuclear vibration, a group of lines appears in the spectrum. With inadequate resolving power of the optical instrument, this group appears as a vibrational band whose centre lies approximately at the position of the line corresponding to the pure vibrational process. As long as one is concerned only with ascertaining how many vibrational frequencies in a molecule occur in the infra-red, an observation of this kind suffices. As soon as it is desired to ascribe the observed frequencies to particular vibrational processes in the molecule, however, an analysis of the rotational structure of the vibrational band cannot be dispensed with. In this, something is also learnt simultaneously concerning the rotational energies which are combined with the vibrational energies, so that such an analysis can replace direct observation of the rotation spectrum.

Classification of the Nuclear Vibrations. — In the case of the rotation-vibration spectra, there are thus two tasks to be accomplished in turn. The first consists of recognizing which nuclear vibrations are possible, and which of them are active and which inactive in the infra-red. Here again, only those are active which generate a periodically changing exterior field by displacement of the nuclei. These include all those changes in the positions of the nuclei in which the *dipole moment changes*. With respect to active rotational vibrations, the molecule itself need not possess a dipole moment, but must, if it be non-polar, assume such through the nuclear vibration, in order that it may interact with the infra-red radiation. This will be illustrated by a few examples.

Symmetrical diatomic molecules like H_2 , O_2 , N_2 and Cl_2 , even when the nuclei vibrate reciprocally, remain centrosymmetric and consequently have a zero dipole moment for every position of the nuclei. They therefore do not give rise to a vibration spectrum. If in such cases it is desired to study the nuclear vibrations, other methods must be adopted.

The two molecules N_2 and CO , otherwise so similar in their physical properties (p. 420), are sharply differentiated by the fact that, on account of the asymmetry of CO , the latter provides a vibration spectrum while nitrogen does not.

The linear carbon dioxide molecule can carry out three modes of nuclear vibrations, namely a symmetric vibration in the direction of the longitudinal axis of the molecule, an antisymmetric vibration along the same axis, and a vibration of the atoms perpendicular to the longitudinal axis, in which the linear form of the molecule becomes bent (Fig. 38). Since all the directions perpendicular to the longitudinal axis are equivalent, all the vibrations taking place in these directions have the same energy, that is to say, they are "degenerate". Each of the other complicated vibrational movements possible can be attributed to these *normal vibrations*, its energy being repre-

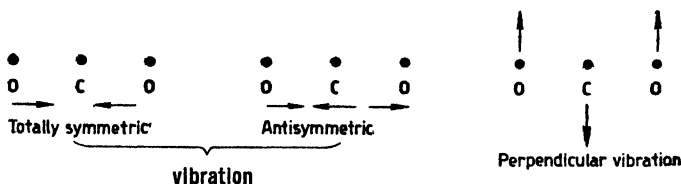


Fig. 38. Vibrations of carbon dioxide.

sented by the sum of the energies of the normal vibrations. It is characteristic of a normal vibration that all the atoms carry out a linear motion with the same frequency and in the same phase, so that they all pass through their positions of rest simultaneously and simultaneously attain their maximum distances therefrom.

Of the normal vibrations, the totally symmetric (in general, a totally symmetric vibration is one in which the symmetry of the molecule is not changed), in which the two similarly bound oxygen atoms vibrate towards the centre (and away from it), is inactive, since in this case the CO_2 molecule retains its zero dipole moment. By contrast, with the antisymmetric vibration, which is so called because on reflection at the carbon atom all displacements of the nuclei reverse their sign, the molecule obtains a moment, as is immediately apparent. Likewise, the opposed vibrations of the carbon atom and two oxygen atoms perpendicular to the longitudinal axis lead to a deformed bent molecule with a dipole moment. Both of these other normal vibrations are therefore active. The nitrous oxide molecule, like that of carbon dioxide, is linear. Nevertheless, it exhibits the frequencies in the infra-red spectrum corresponding to all three normal vibrations. In this case, therefore, no vibration is inactive. It must consequently have the unsymmetrical structure $\text{N}\equiv\text{N}=\text{O}$ and could not possess the structure $\text{N}-\text{O}-\text{N}$. Its dipole moment is certainly so small, that it would not have been possible to decide with certainty upon the unsymmetrical structure because of it: from the infra-red spectrum, this is possible.

As a further example of a compound with active and inactive vibrations, methane CH_4 might be mentioned. Its normal vibrations are reproduced in Fig. 39. The vibration *a*, a so-called *pulsation*, is totally symmetric, while *b*, although not totally so, is however centrosymmetric. Both are inactive. The vibrations *c* and *d* are antisymmetric and active.

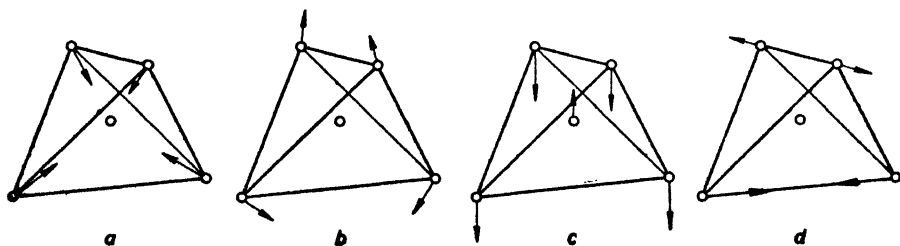


Fig. 39. Vibrations of methane

The frequencies of the vibrations depend upon the forces which tend to keep the atoms in their positions of rest and consequently provide a measure for the *strength of binding* between them. However, only in the case of relatively simply constructed molecules with certain symmetry properties, like carbon dioxide, is it possible to describe the individual vibrational processes in such a way as to be able to ascribe to the individual frequencies *force constants* that are unequivocally related to the strengths of particular bonds. On account of the number of vibrational degrees of freedom, one usually needs more force constants to describe the vibrations than there are frequencies occurring in the molecule, in which case an unambiguous derivation of the force constants from the frequencies is not feasible. In such cases, it is sometimes possible to increase the number of determinative equations by the required figure through including the frequencies of the compounds containing isotopes of the elements.

Theoretically, the forces which tend to restore the atoms to their positions of rest can, in first approximation, be treated as classical and quasi-elastic forces, the nuclear vibrations being thereby regarded as harmonic vibrations. A molecule thus behaves like a model constructed of spheres held together by springs: this is the so-called *spring model* which, in spite of its imperfect nature, has performed good service in the interpretation of characteristic infra-red frequencies.

In the case of carbon dioxide, two kinds of vibrations can be distinguished from the standpoint of the quasi-elastic binding of atoms, namely those in the direction of the line joining the nuclei, with which the interatomic distances change, and those at right angles thereto. Since, in a structural formula, a valence-dash is written along the line joining two atoms, vibrations which take place along this direction are termed *stretching* or *valence vibrations*⁹⁸, and the others, with which a "bending" of the valence-line occurs, *bending* or *deformation vibrations* (Fig. 40). The latter have

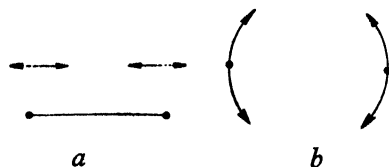


Fig. 40. (a) Stretching (valence) and (b) bending (deformation) vibrations

altogether smaller frequencies than the former, that is, it takes more work to displace two atoms towards or away from one another than to move them perpendicular to the line which joins them with only a slight change of the intervening distance. In accordance with the model, one will be inclined to interpret the force constant for the stretching vibrations as the elastic

⁹⁸ R. МЕСКЕ, *Z. Elektrochem.*, 1930, **36**, 593.

force of "valency". For identical bonds, therefore, such "valence forces" would have to be the same. Carbon dioxide again provides a testing ground for this, since it can carry out two valence vibrations, the totally symmetric and the antisymmetric. The frequencies of these two vibrations, of which the former admittedly cannot be obtained from the infra-red spectrum⁹⁹, do indeed permit of calculation with a good degree of approximation from one and the same force constant. That the force constants found for C=O bonds in organic compounds turn out to be somewhat — though by no means greatly — different¹⁰⁰ than for carbon dioxide is not surprising, on account of the strong reciprocal influencing of the two "double bonds" in the latter (p. 426)¹⁰¹.

Great as is the value which the spring model has on the whole for calculations serving to provide a survey of forces extant between atomic nuclei, it is nevertheless, as is easily understood, not applicable as basis for an exact calculation of the frequencies. Simply for the sake of indicating one point where it is inadequate, it might be mentioned that the harmonic nature of stretching vibrations which follows from it does not in reality exist: namely, the work required to bring two atoms closer to each other by a small distance is in general greater than that which must be expended to increase their distance by the same small amount. With the mechanical spring, on the other hand, the work of compression and stretching are equivalent to each other.

(v) The Rotational Structure of Vibration Spectra

The selection rules which forbid the occurrence of certain vibrations in the infra-red permit, as far as the observed infra-red frequencies are concerned, vibrations of a certain symmetry to appear as excluded. In this, however, apart from very rare cases, an ascription of a particular frequency to a particular vibrational process has not yet been given. In carbon dioxide, for example, the two observed¹⁰² infra-red frequencies 2.0 and 7.1×10^{13} sec^{-1} or the wave numbers 677 and 2370 cm^{-1} are not, without any further consideration, to be attributed to the two active vibrations. Here, it is true, the experience that stretching vibrations generally have higher frequencies than bending vibrations can be drawn upon for a decision: nevertheless,

⁹⁹ To be sure, it can be obtained in a not very simple manner from the RAMAN effect, with respect to which it is not inactive. In this particular case, the state of affairs is complicated in that, instead of the "frequency" 1321.7 cm^{-1} , two "frequencies" appear, which originate from an interaction between the totally symmetrical vibration and the first overtone of the "vertical vibration" of frequency $2 \times 667 = 1334$ cm^{-1} : E. FERMI, *Z. Physik*, 1931, **71**, 250.

¹⁰⁰ Regarding the variation in force constant for the C=O link, see A. D. WALSH, *Trans. Faraday Soc.*, 1947, **43**, 158.

¹⁰¹ For an early compilation of partly calculated, partly estimated stretching force constants, see G. B. B. M. SUTHERLAND, *Ann. Rep. Chem. Soc.*, 1936, **33**, 64. For more recent data, see G. HERZBERG's *Infrared and Raman Spectra* (Van Nostrand, New York, 1945).

¹⁰² The inactive vibration has $\nu = 38 \times 10^{13}$ sec^{-1} or $\tilde{\nu} = 1322$ cm^{-1} .

this experience had first to be gained from numerous examples, and that has been possible only by analysis of the rotational structures of vibration spectra.

We thus turn now to the second task which the rotation-vibration spectra provide for research.

The analysis of the rotation-vibration spectra of *diatomic molecules* is straightforward.

The nuclear vibrations which bring about the changes in moment necessary for the appearance of the spectrum here occur in the direction of the line joining the atoms. Simultaneously the molecule rotates about an axis perpendicular to this. Its direction is furthermore immaterial, since all directions at right angles to the line joining the atoms are equivalent. The classical treatment of a vibrating rotator of this type demonstrates by a simple calculation¹⁰³ that the variation in moment created by the vibration does not oscillate with the frequency ν_v , corresponding to the vibrational period of the molecule when at rest, but in part with a frequency which is higher by the frequency of rotation and in part with a frequency lower by the same amount, namely $\nu_v + \nu_r$ and $\nu_v - \nu_r$.

The quantum-mechanical treatment of the problem, which enquires into the transitions between the stationary states characterized by the frequencies ν_v and ν_r , leads to a formula for a line series which is quite similar to that given above for the rigid rotator:

$$\nu = \omega_e \pm \frac{h}{4\pi^2 c I} (m'' + 1) \quad (m'' = 0, 1, 2, 3, \dots)$$

The quantity ω_e , which is absent in the formula valid for the rigid rotator, here signifies the wave number, extrapolated with integral vibrational quantum numbers, that refers to the harmonic oscillator which corresponds to the nuclear vibration.

According to this formula, a sequence of equidistant lines which group themselves symmetrically about the frequency of nuclear vibration are thus to be expected. This nuclear vibration does *not* however appear with its own frequency exactly as in the classical presentation; for the quantum number m'' cannot assume the value -1 as is necessary in order to make the "correction term" due to rotation vanish, so that ν becomes equal to ω_e . The line series possessing frequencies higher than the nuclear vibration is referred to as the positive or *R* branch, that with lower frequencies as the negative or *P* branch.

If one compares the observed rotation-vibration spectra of diatomic molecules, *e.g.*, the fundamental vibrational band of hydrogen chloride¹⁰⁴, with the demands of the theory, one finds in accordance with the latter that the nuclear vibration itself is missing, and that spectral lines group them-

¹⁰³ A. EUCKEN, *Lehrbuch der chemischen Physik*, Vol. I, p. 438 (2nd Ed., 1938).

¹⁰⁴ E. S. IMES, *Astrophys. J.*, 1919, 50, 251.

selves about it on both sides (see Fig. 41). But these lines do not have the same separation. Rather, the latter diminishes regularly with increasing frequency. Consequently the lines in the *R* branch lie closer together than in the *P* branch. The reason for this lies in the derivation of the formula, which

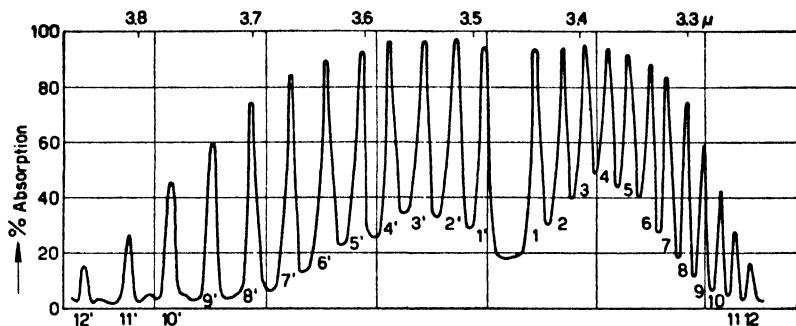


Fig. 41. Fundamental vibrational band of hydrogen chloride

originally neglected an interaction between vibration and rotation, and in which the rotational energy of a vibrating dipole depends namely not only on the rotational quantum number, but also on the vibrational quantum number. This dependence is of such a kind that the moment of inertia increases with increasing vibrational energy. Consideration of this factor leads to a correction of the simple formula given above, after which the theory henceforth agrees excellently with experiment.

In the case of molecules with more than two atoms, the theory of the rotational structure of the vibration spectra becomes more involved. It may therefore suffice if carbon dioxide is taken as example. Here the state of affairs is particularly simple, since in its state of rest the molecule is linear. With such molecules the expression for the rotational energy is the same as for diatomic molecules. Vibrations in the direction of the molecular axis that bring about a change in the moment, like the antisymmetric vibration in carbon dioxide, correspond completely to the nuclear vibrations of diatomic molecules. Consequently the rotational structure of the bands derived from such vibrations must be the same as in the case of diatomic molecules.

For vibrations perpendicular to the molecular axis, this does not hold. Only if the rotational axis (in addition to the molecular axis) is likewise perpendicular to the change of moment, will the frequency of this change vary by the same amount as in the case of vibrations along the molecular axis, and — in the classical representation — instead of ν_v the two frequencies $\nu_v + \nu_r$ and $\nu_v - \nu_r$ appear. If, on the other hand, the rotational axis lies in the direction of the change of moment, then the frequency corresponding to the latter will not be altered at all by rotation. Or, presented rather diff-

erently, if the molecular axis is perpendicular to the change in moment, there are two limiting cases to consider:

- (a) rotational axis \perp change in moment;
- (b) rotational axis \parallel change in moment.

(a) The $\text{O}=\text{C}=\text{O}$ molecule lies along the x axis with the carbon atom at the origin. The molecular axis is thus the x axis. Now suppose a vibration occurs in which the carbon and the two oxygen atoms vibrate in the opposite direction but perpendicular to the molecular axis, say in the xy plane, so that, with the specified position of the molecule, the C atom moves up and down along the y axis. The periodically changing moment therefore lies in the direction of the y axis. If, on top of this vibration, a rotation perpendicular to the two directions should now take place about the z axis, then the change in frequency through rotation would be the same as when the vibrations occurred along the x axis.

(b) If, however, the rotation now occurs about the y axis, this does not change the frequency, for points lying on the y axis retain their position during rotation. The case is the same as when a dipole rotates about its own axis, such a rotation generating no periodically changing field and contributing nothing to the rotation spectrum.

In the former limiting case, the proper frequency of nuclear vibration disappears as for a diatomic molecule, in the latter it remains preserved.

In general, if the axis of rotation and the direction of change in moment make any given angle with one another, then the change in moment can be resolved into two components, one perpendicular to the rotational axis leading to the frequencies $\nu_v \pm \nu_r$, and one parallel to it, which results in the frequency ν_v . Since, on taking an average over all the possible directions, the components vertical and parallel to the axis of rotation are equally abundant, the sum of the intensities of all the $\nu_v + \nu_r$ and $\nu_v - \nu_r$ lines in the R and P branches must be equal in intensity to the ν_v line.

With such "perpendicular vibrations", like the one the CO_2 molecule is able to perform, an intense line must therefore occur between the P and R branches which corresponds in frequency to the nuclear vibration. This is the so-called Q branch. In the case of carbon dioxide, this is observed in the vibrational band lying at 677 cm^{-1} ¹⁰⁶ (see Fig. 42). This band must therefore be the "perpendicular band" of carbon dioxide. The other band which is observed with carbon dioxide has no Q branch, it representing the asymmetric vibration. In this way, the bands of carbon dioxide can be unambiguously attributed to the possible modes of vibration.

Also for polyatomic molecules which may be treated as symmetrical tops, vibrational bands, which correspond on the one hand to vibrations *along* and on the other to vibrations *perpendicular to* the axis of symmetry, may be clearly distinguished by their rotational structure. The bands observed for

¹⁰⁶ P. E. MARTIN and E. F. BARKER, *Phys. Rev.*, 1932, [ii], 41, 291.

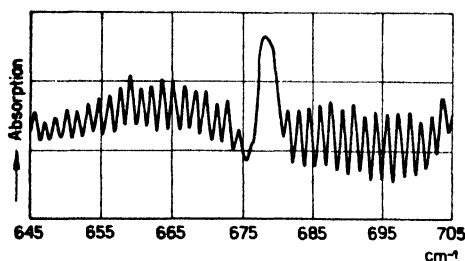


Fig. 42. Q branch additional to the P and R branches in the perpendicular band of carbon dioxide

methyl chloride, namely the “parallel band” corresponding to a change in moment in the direction of the threefold axis and the “perpendicular band” in which the vibration effects a change of moment perpendicular to this axis, provide an illustration of this ¹⁰⁶ (see Fig. 43).

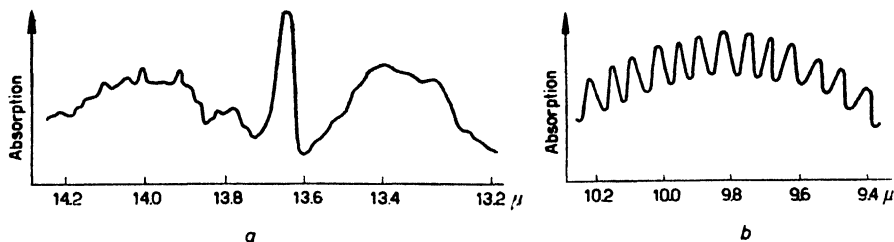


Fig. 43. (a) Parallel and (b) perpendicular bands of methyl chloride

That it is possible to calculate the rotational frequencies from the separation of the lines in the rotation-vibration spectrum and hence the moments of inertia, needs to be mentioned only briefly here. It may likewise suffice to mention the fact that the lines in the electronic band spectra in the visible and ultra-violet regions also possess a rotational structure which can be analyzed and employed for the calculation of rotational frequencies.

7. The RAMAN Effect ¹⁰⁷

(i) Significance of the RAMAN Effect

The frequencies in the infra-red, a knowledge of which is important for the calculation of force constants and moments of inertia, can be derived

¹⁰⁶ W. H. BENNETT and C. F. MEYER, *Phys. Rev.*, 1928, [ii], **32**, 888.

¹⁰⁷ K. W. F. KOHLRAUSCH, *Der Smekal-Ramaneffekt, Struktur der Materie*, Vols. XII and XIX (Springer, Berlin, 1931 and 1937); *Hand- und Jahrbuch der chemischen Physik*, Vol. VI/9 (Akad. Verlagsges., Leipzig, 1943); G. PLACZEK, *Rayleigh-Streuung und Ramaneffekt, Handbuch der Radiologie*, Vol. VI/2 (Akad. Verlagsges., Leipzig, 1934); G. B. B. M. SUTHERLAND, *Infrared and Raman Spectra*, (Methuen, London, 1935); G. HERZBERG, *Infrared and Raman Spectra of Polyatomic Molecules* (Van Nostrand, New York, 1945); J. H. HIBBEN and E. TELLER, *The Raman-Effect and its Chemical Applications*, (Am. Chem. Soc. Monograph No. 80, Reinhold, New York, 1939); J. H. HIBBEN, *Chem. Rev.*, 1936, **18**, 1; J. GOUBEAU, *Physikalische Methoden der analytischen Chemie*, Part III, p. 263 (Leipzig, 1939).

directly in ways other than from the rotational structure of the electronic band spectra. In the scattering of visible light, as C. V. RAMAN first observed in 1928, there occurs in addition to the scattering process caused by density variations in the medium — the RAYLEIGH scattering, which has no modifying effect on the frequency of the incident light — yet another scattering process, which is dependent on the material nature of the scattering medium and yields light of frequencies which are close to that of the incident light. Accordingly, a *spectrum* arises from monochromatic incident light which contains in addition to the strong line of frequency equal to that of the incident light, the RAYLEIGH line, a series of weak satellites, the RAMAN lines. The frequency differences $\Delta\nu$ between the principal line and its satellites correspond to the characteristic infra-red frequencies of the substance scattering the light. They are independent of the frequency of the monochromatic incident light. In general, the RAMAN lines lie at longer wave-lengths than the exciting line. More rarely, RAMAN lines with shorter wave-lengths also occur.

The RAMAN effect supplies the infra-red frequencies, and that in an experimentally much more convenient way than the direct observation of the infra-red spectrum, since one can here work with visible light. But, for the most part, it is not possible to resolve the characteristic infra-red frequencies resulting from the frequency differences $\Delta\nu$ to the point where an analysis of the rotational structure of the respective vibrational band can be undertaken. The intensity of the RAMAN lines is usually too small for the resolution. Also, because of the meagre intensities, the overtones from which one can obtain details about the symmetry properties of the vibrations are found only rarely. On the other hand, the possibility exists of gaining knowledge about the latter from the polarization properties of the RAMAN lines. Under certain circumstances, a measurement of the degree of depolarization of a RAMAN line enables the attribution of an observed frequency to a normal vibration to be made with more certainty.

However, the significance of the RAMAN effect does not lie solely in the fact that, because of it, a knowledge of the characteristic infra-red frequencies of molecules is obtained by experimental paths which are more convenient than a direct determination. Namely, under certain circumstances, it also enables one to gain a knowledge of infra-red vibrational frequencies which, as inactive vibrations, are not available for direct interaction with infra-red radiation. To be sure, there are also selection rules with the RAMAN effect, in consequence of which certain vibrations are inactive by virtue of particular symmetry relationships, but these are other than for infra-red absorption. Thus, for example, the totally symmetric pulsation of the CH_4 molecule is inactive in the infra-red spectrum and active in the RAMAN spectrum. Thus infra-red investigations and RAMAN spectroscopy *supplement* one another.

The general theory of the RAMAN effect, which in its essential outlines

had already been given by SMEKAL 5 years before RAMAN's discovery, will be sketched only very briefly here; for it is not so material, in relation to what follows, how in addition to ordinary coherent scattered radiation — TYNDALL or RAYLEIGH scattering, which is mostly in phase with the incident light — yet another incoherent (that is, not vibrating in phase with the incident light) scattering, namely RAMAN scattering of frequency differing from that of the incident light, should be possible. It is much more important to recognize the symmetry restrictions which the molecule must fulfil, in order that the vibrations peculiar to it should appear in the RAMAN spectrum. For this, a detailed knowledge of the quantum theory of the RAMAN effect is not required.

(ii) Quantum Theory of the RAMAN Effect¹⁰⁸

An atom or a molecule is capable of existing in different discrete stationary states. If it interacts with a light wave of frequency ν which does not coincide with one of its own characteristic frequencies — the case of selective absorption will be left out of consideration here — it is able to take up the energy $h\nu$. Since the state attained by the assumption of this energy is not a stationary state, the atom or molecule again reverts to a stationary state. If this is the original state, the energy emitted is equal to that temporarily absorbed, and the frequency ν remains the same. This is the case for coherent scattering. Alternatively, as is the case for RAMAN scattering, the second stationary state can differ from the initial state. Either it is poorer in energy than the initial state — this being possible only if the latter was an excited state — when more energy is radiated than was absorbed, or the molecule remains in a state richer in energy than that in which it was originally, when less energy is emitted than was taken up. In the former case, the emitted energy is $h\nu + h\nu_{kj}$, in the latter $h\nu - h\nu_{kl}$, in which the subscript k signifies the initial state, j a stationary state of lower energy and l one of higher energy. The frequencies of the emitted energies are thus respectively

$$\nu_+^* = \nu + \nu_{kj} \quad \text{or} \quad \nu_-^* = \nu - \nu_{kl}.$$

These are the RAMAN frequencies.

The larger the differences in energy between the stationary states k and j or l , the more the frequency of the incident light is changed. Of the various vibrations possible in the molecule or atom, the nuclear vibrations in the infra-red with their low frequencies mean only small differences in energy. In the molecule, such stationary states thus lie energetically close to one another, and are differentiated by the energies of nuclear motion — vibration and rotation. Hence, when the molecule or atom has temporarily taken up energy and does not revert to the initial state, lines will be emitted which differ from the energy $h\nu$ of the incident light by the energies of these nuclear

¹⁰⁸ Treated in greater detail in text-books and in W. HÜCKEL's *Theoretische Grundlagen der organischen Chemie*, Vol. II, p. 113 ff (5th Ed., 1948).

vibrations. The energy of nuclear motion is obtained from the difference in energy of the incident light and the RAMAN frequencies. Correspondingly, the characteristic infra-red frequencies can also be calculated according to the equations

$$\nu_{kj} = \nu_+^* - \nu \quad \text{and} \quad \nu_{kl} = \nu - \nu_-^* .$$

(iii) Selection Rules for the RAMAN Effect

It can be seen from the theory of the RAMAN effect, that with this phenomenon an interaction between radiation and the characteristic infra-red vibrations themselves does not occur. For the RAMAN lines, therefore, other selection rules hold than for the lines in the infra-red spectrum. In order, with regard to these rules, to find out whether a vibration is active for the RAMAN spectrum or not, one must ask oneself which nuclear movements are able to influence the process of light scattering. For this, one must know which factors in the structure of the molecule are at all determinative for the scattering of light.

The ordinary coherent TYNDALL scattering arises from the fact that the scattering molecules in a gas or liquid are unequally distributed. The intensity of scattered light depends upon the wave-length¹⁰⁹ — light of short wave-length is scattered more than light of long wave-length — and upon the polarizability of the molecule. If the molecule is not spherically symmetrical, a further factor comes into the picture, namely the anisotropy of polarizability. If the polarizability is not the same in all directions of the molecule, part of the scattered light is depolarized, and that in an amount dependent upon the inequality of polarizability in the different directions.

Polarizability and anisotropy of polarizability therefore enter as constitutive peculiarities of a molecule into the intensity of the scattered light. Consequently it is to be expected that the nuclear movements which are of influence on the light scattering and hence appear in the RAMAN effect are those which change the polarizability or anisotropy of polarizability, or which influence the orientation of a molecule which is not spherically symmetrical. In this, as in the case of infra-red spectra, it is useful to keep the processes of rotation and nuclear vibration separate and differentiate between a rotational RAMAN effect and a vibrational RAMAN effect.

(iv) Rotational RAMAN Effect

If a spherically symmetrical molecule or atom rotates, the field of force radiating from it is exactly the same as for the rest state. Rotation can therefore exert no influence upon the scattering of light. Spherically symmetrical molecules like methane and carbon tetrachloride thus give no *rotational* RAMAN effect. If, on the other hand, the molecule possesses polarizabilities

¹⁰⁹ The energy of the scattered light is proportional to the fourth power of the frequency ν .

which differ in different directions, then, in the most general case, the surrounding force field changes periodically as it rotates with a frequency equal to that of rotation. In the RAMAN effect involving an occurrence of interaction between the radiation and molecule during the scattering process, this is able to add to (or also subtract from) the frequency of the incident light.

In the most general case, in which the polarizability of the molecule can be represented by an ellipsoid of polarization with three different principal axes, there are, as is easily comprehensible, a total of three rotations about these principal axes active in the RAMAN spectrum, since with respect to each the field about the molecule changes periodically. The scattered radiation is incoherent with the incident light, since the phase of rotation is independent of that of the latter.

If the molecule possesses special symmetries, selection rules hold for it. If two axes of the ellipsoid of polarization are equal, it thus becomes an ellipsoid of rotation, so that rotation of the molecule about its axis of rotation does not affect the field and is consequently inactive as a rotational vibration. Rotation through a complete turn of 360° about any given axis perpendicular thereto brings the ellipsoid of rotation twice into congruence with its original position. A periodically alternating field is thus generated, as a result of which RAMAN lines are produced whose frequency with respect to that of the incident light is displaced by double the rotational frequency. Thus the distance between the RAMAN lines here corresponds not to the characteristic infra-red frequency ν_r , but to $2\nu_r$. Examples of such molecules are the diatomic molecules of elements and symmetrical linear molecules like CO_2 or carbon suboxide $\text{O}=\text{C}=\text{C}=\text{C}=\text{O}$. All these yield no infra-red rotation spectrum. Since the diatomic molecules of the elements do not exhibit an infra-red absorption spectrum at all, the possibility exists in the case of these molecules of gaining a knowledge of the characteristic infra-red frequencies by means of the RAMAN effect and hence, as in the case of the nitrogen molecule, for example, of calculating the moment of inertia.

If the molecule is a symmetrical top — thus possessing an axis of symmetry but no centre of symmetry — like NH_3 and CH_3Cl , for example, rotation about the axis of symmetry is inactive in the RAMAN spectrum, as it is in the infra-red. Rotation about any other given axis yields, as mentioned earlier (p. 357), a precession in which the position of the ellipsoid of polarization changes in space. A rotation of this kind is consequently active in the RAMAN effect. Here, also, the ellipsoid of polarization is in special cases able to come into congruence with itself by a precession after rotating through only 180° ; but in general this is only the case after a complete revolution of 360° . For such molecules, therefore, other than for symmetrical diatomic molecules, the single rotational frequencies make their appearance together with the double in the RAMAN effect. There are thus two series of lines which are superimposed in such a way, that upon each second line of the

first series a line of the second series falls, whereby each alternate line in the RAMAN spectrum appears as reinforced.

(v) Vibrational RAMAN Effect

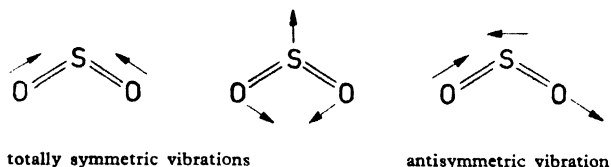
Most of the RAMAN lines are attributable to nuclear vibrations, by which the force field surrounding the molecule is modified if they change the polarizability of the molecule. Only those vibrations which change the polarizability are active in the RAMAN effect. If in normal vibration, during which all the atoms simultaneously pass through their equilibrium positions, the polarizability has a maximum or a minimum, then for a virtual displacement the change in polarizability — the first differential of polarizability with respect to the displacement — is equal to zero. The corresponding vibration is thus inactive in the RAMAN effect. According to this point of view, it is possible to draw up selection rules which are valid for molecules with particular symmetry properties. To enumerate them all here would lead too far afield¹¹⁰. It may suffice to consider the case of methane. In methane the totally symmetric vibration, the pulsation, is active in the RAMAN effect, because with the even approach of the hydrogen nuclei to the carbon atom the polarizability changes. The corresponding RAMAN lines do not show a rotational structure, since the molecule remains spherically symmetrical during the pulsations. By contrast, the other three normal vibrations (p. 361, Fig. 39), which are likewise active, possess rotational structures, since for them the polarizability does not remain spherically symmetrical during the vibrations, but becomes anisotropic: that is, they are all unsymmetrical in some or other element of symmetry.

The lines corresponding to pulsation can be recognized as such by the absence of a rotational structure. Since, however, the RAMAN lines do not in general become resolved to the extent that their fine structure becomes capable of analysis, only in rare cases will it be possible to draw upon rotational structures for ascribing a particular line to a particular vibration.

It is therefore important that there should also be yet another classifying principle which, experimentally, is more easily accessible, namely depolarization of the RAMAN lines. A totally symmetric vibration, for which the symmetry is identical at every instant, does not possess an anisotropic factor for scattered radiation any more than a spherically symmetrical molecule with respect to coherent radiation. The RAMAN line corresponding to this must therefore be completely polarized. For the antisymmetric normal vibrations of methane, as can be deduced from the theory of depolarization of scattered radiation, the degree of depolarization must be the largest possible with a value of $\frac{3}{4}$. The value observed is 0.8. This also holds for antisymmetric normal vibrations in other molecules, as, for example, in sulphur dioxide. The two other normal vibrations of the sulphur dioxide molecule,

¹¹⁰ An enumeration is to be found in G. PLACZEK's *Rayleigh-Streuung und Raman-effekt*, *Handbuch der Radiologie*, Vol. VI/2, p. 315 ff (2nd Ed., 1934).

although totally symmetric, are not spherically symmetrical. On account of the absence of spherical symmetry of polarizability, they likewise exhibit a depolarization, which is however essentially smaller than the maximum value.



There is finally still a third possibility of assigning the RAMAN frequencies to definite vibrations. In this, one proceeds from the spring model, and, with certain simplifying assumptions concerning the elastic forces, calculates the vibrational frequencies for the individual vibrations in order to discover which of the observed RAMAN frequencies lie near to these. This method is however only applicable to molecules of relatively simple structure, for which calculations with models can be undertaken without any too daring hypotheses¹¹¹.

(vi) Application of the RAMAN Effect

By far the most general application of RAMAN spectroscopy consists in assigning the lines observed in photographs of RAMAN spectra to definite bonds, as far as this should be possible. If the same or nearly the same frequency occurs again in different compounds, it can be assumed that they contain the same linkage. From the dimension of the frequency, it is possible to make conclusions concerning the strength of the relevant bond, and compare this with the strength of other bonds. Only in relatively rare cases does the analysis of a RAMAN spectrum extend to the point where it leads to the derivation of the form of the molecule. A few examples may throw light on the various ways in which the RAMAN effect can be utilized for research into the constitution of inorganic compounds¹¹².

The RAMAN effect has provided a possibility of determining the nuclear frequencies of symmetrical molecules of diatomic gases. In this it is seen that the force constants increase appreciably in the series H_2 , O_2 , N_2 , that is, the bonding becomes stronger. If the magnitudes of the force constants are compared with those for carbon atoms in single, double and triple bonds in hydrocarbons, then the order of magnitude observed for the force constant of the hydrogen molecule agrees with that of the single bond, for the oxygen

¹¹¹ Cf., e.g., K. W. F. KOHLRAUSCH, *Österr. Chem. Ztg.*, 1939, **42**, 345; reproduced in W. HÜCKEL's *Theoretische Grundlagen der organischen Chemie*, Vol. II, p. 128 (5th Ed., 1948).

¹¹² Further examples are to be found in the compilation of A. SIMON, *Z. angew. Chem.*, 1938, **51**, 783; 808. This includes a comprehensive citation of references in the literature, which are therefore not all repeated in what follows. RAMAN spectrum and ionization of $HClO_4$, which is stronger than that of HNO_3 ; O. REDLICH, E. K. HOLT and J. BIGELEISEN, *J. Am. Chem. Soc.*, 1944, **66**, 13; cf. R. FONTEYNE, *Nature*, 1936, **138**, 886; *Naturw. Tijdschr.*, 1938, **20**, 112. An OH and two O bands are here superimposed, which has rendered the interpretation more difficult.

molecule with that of the double bond, and for the nitrogen molecule with that of the triple bond. In addition, a force constant results for the nuclear vibration of carbon monoxide which is not so very far removed from that of the $C\equiv C$ triple bond. As a consequence, one will be disposed to write these molecules $H-H$, $O=O$, $N\equiv N$ and $C\equiv O$, in which one makes use of the same symbolism as in organic chemistry.

Whether, however, the bonds are really of the same kind cannot be stated from the RAMAN effect, since this does not comprise the states of the electrons. One can only say that the strengths of the bonds are about the same. With that, the bonding "mechanism" may be completely different. One can thus draw conclusion concerning similarity of bond type only with reserve.

If a frequency or group of frequencies recurs in several compounds, possibly with small displacements, the presence of a particular group of atoms can be inferred. One then speaks of *group frequencies*. Thus, for the most varied of hydroxyl compounds, in which the presence of a hydroxyl group has been ascertained from chemical reasons, a "frequency"¹¹³ lying at about 3500 cm^{-1} is observed. If this should appear with a compound for which a hydroxyl group could not be demonstrated in other ways, it could from this be assumed that a hydroxyl group were present in the molecule, provided, in this manner of reasoning, that the RAMAN frequencies of the group were only slightly influenced by the groups with which it is linked. Otherwise, it can happen that, as a result of strong interaction, the frequency of a strongly influenced group is displaced to such an extent that it is not recognizable. One must also guard against possible errors through the coincidence of frequencies of different groups, and ascertain the absence of such coincidences by special observations.

Examples for the detection of the presence of a particular group are provided by the anhydrous inorganic oxy-acids, whose formulae can be written either with hydroxyl groups to correspond with the organic structural formulae of their esters, or in a heteropolar manner in accordance with WERNER, that is, for the example of nitric acid, either $HO-NO_2$ or $H[NO_3]$. Conclusions are admittedly rendered more difficult on account of the fact that different species of molecules can be present in the anhydrous liquid acid.

Anhydrous liquid nitric acid possesses in its RAMAN spectrum a band a little below the frequency 3500 cm^{-1} (see Fig. 44), which is characteristic for hydroxyl compounds. In addition, a number of lines are observed which are otherwise found for nitro-compounds and nitrites. From this, the presence of homopolar molecules with the structure $HO-NO_2$ can be concluded with a high degree of certainty. However, these are not exclusively present, since, even if only weakly, a line attributable to the nitrate ion NO_3^- occurs. This increases in strength on dilution of the nitric acid, during which the frequencies of the OH and NO_2 groups simultaneously weaken. This change finds a natural explanation in an increasing dissociation of the acid. The

¹¹³ Concerning the expression "frequency", see p. 356, footnote 94.

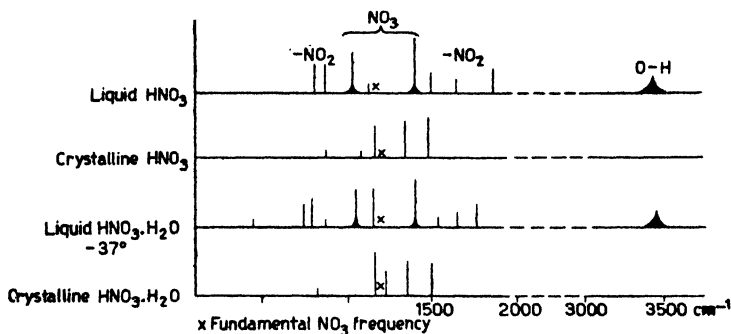


Fig. 44. RAMAN spectrum of nitric acid

presence of the NO_3' frequencies in the anhydrous acid is perhaps not attributable to a substance of formula $\text{H}[\text{NO}_3]$, but to an autocomplex in which the proton is linked to HNO_3 , possibly $\left[\begin{array}{c} \text{H} \\ \text{HO}-\text{NO}_2 \end{array} \right] \text{NO}_3$. Crystalline anhydrous nitric acid does not give the hydroxyl band: the NO_2 lines are also not to be identified with certainty. On the other hand, the lines characteristic of NO_3' are strong. In the crystalline acid, therefore, the lattice probably possesses an autocomplex structure. Nitric acid monohydrate in the crystalline state has a spectrum which is only slightly different, likewise with strong NO_3' lines and without an OH band. It is thus to be formulated as hydroxonium nitrate $[\text{H}_3\text{O}]\text{NO}_3$. In the molten state it also shows the hydroxyl band and NO_2 lines, so that it then represents a mixture of H_3O^+ , NO_3' , $\text{HO}-\text{NO}_2$ and H_2O .

In the case of sulphuric acid, the state of affairs is similar to that for nitric acid, which is not surprising. By way of contrast, a hydroxyl band is *not* observed with anhydrous orthophosphoric acid H_3PO_4 , whereas lines which are also found in tripotassium phosphate are. PO_4''' ions are thus present in the acid. The poverty of the spectrum (Fig. 45) with regard to lines

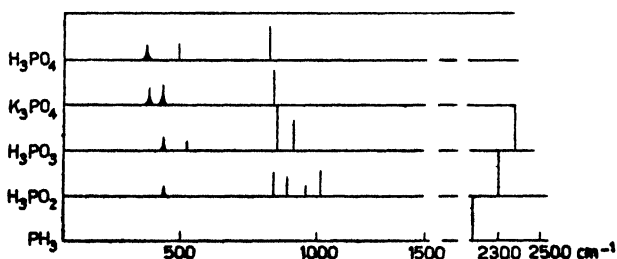
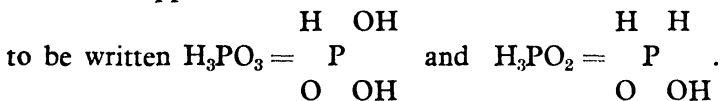


Fig. 45. RAMAN spectrum of phosphoric acid

is in harmony with this, since a tetrahedral PO_4''' ion, in consequence of the selection rules, can give at most four RAMAN lines. This number only is also observed with K_3PO_4 . On dilution, phosphoric acid does not change

its RAMAN spectrum, thus differing in behaviour from nitric and sulphuric acids. As a consequence, it seems natural to assign to it the structural formula of a true acid, namely $\text{H}_3[\text{PO}_4]$, which is however contradicted by its moderate—on more extensive dissociation only weak—acidic nature¹¹⁴. In the liquid acid, apparently only autocomplexes with PO_4''' ions are present, possibly $4\text{H}_3\text{PO}_4 = [\text{P}(\text{OH})_4]_3\text{PO}_4$, but no single $(\text{HO})_3\text{PO}$ molecules. It would seem not to be excluded that the OH frequencies in a complex like $\text{P}(\text{OH})_4'$, which is perhaps to be written $[\text{PO}_2 \cdot 2\text{H}_2\text{O}]'$, are so changed that they are not found. An explanation free from hypotheses cannot be given on the basis of the RAMAN effect. With arsenic acid, in contrast to phosphoric acid, the OH band is found: molecules like $(\text{HO})_3\text{AsO}$ can thus be assumed here.

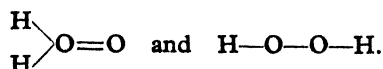
Anhydrous phosphorous and hypophosphorous acids possess spectra recalling that of the phosphate ion, but richer in lines. This agrees well with the supposition that these acids have tetrahedral structures and are



The P—H frequency to be expected from these formulae is also to be observed, but a little displaced with respect to the P—H frequency in phosphine PH_3 . On the other hand, the frequency of the hydroxyl groups occurring in these formulae is strikingly absent in Fig. 45. It appears however possible that autocomplex-formation also causes the hydroxyl-group frequency to disappear here. The representation $\text{H}_2[\text{PO}_3\text{H}]$ and $\text{H}[\text{H}_2\text{PO}_2]$ avoiding hydroxyl groups is again in poor agreement with the weak acidic nature of these acids. As in the case of orthophosphoric acid, the placing—merely by reason of the RAMAN effect—of a proton by the side of the complex as a heteropolarly bound ion also appears risky here, intrinsically plausible as the explanation may seem.

The PO_4''' ion in orthophosphoric acid has already provided an example of how, in assigning frequencies, inferences can be made regarding the symmetry of an atomic grouping. Another simple example is boric acid, for which the OH band is detectable, and which further gives only three RAMAN lines, one of these corresponding to a totally symmetric vibration¹¹⁵. From this, the formula $\text{B}(\text{OH})_3$ follows, the structure being planar and the symmetry trigonal.

A more complicated example is provided by hydrogen peroxide. Two tautomeric formulae were still being discussed for this compound in 1932, namely

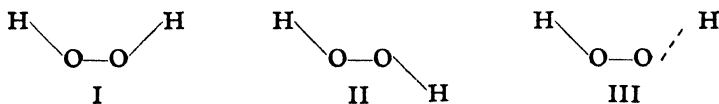


¹¹⁴ A. SIMON (*loc. cit.*, footnote 112) omits to mention this contradiction, and writes $\text{H}_3[\text{PO}_4]$ without considering the possibility of autocomplex formation.

¹¹⁵ R. ANANTHAKRISHNAN, *Proc. Indian Acad. Sci.*, 1936, A 4, 74; 1937, A 5, 200; J. C. GHOSH and S. K. DAS, *J. Phys. Chem.*, 1932, 36, 586.

The RAMAN spectrum shows the hydroxyl band at 3400 cm^{-1} and a frequency at 877 cm^{-1} which, according to its position, can only be attributed to a single bond, that is to say, it must be assigned to an O—O bond. In addition, yet another frequency appears at 1421 cm^{-1} , which lies not far from the frequencies occurring for double bonds. This may however refer to the frequency of a deformation vibration of the two hydrogen atoms. The RAMAN spectra of deuterium peroxide D_2O_2 and deuterium hydroperoxide HDO_2 are able to effect a decision between the two possibilities. If the frequency 1421 cm^{-1} belongs to an O=O valence vibration, on the substitution of hydrogen by deuterium it will change only slightly. If, on the other hand, it corresponds to a deformation vibration of the two hydrogen atoms, it must be strongly displaced. The latter is observed to be the case. In D_2O_2 it disappears, and its place is taken by a frequency at 1009 cm^{-1} . In addition, instead of the OH frequency at 3400 the OD frequency at 2510 cm^{-1} is observed. The reduction of the frequency at 1421 to 1009 cm^{-1} exactly corresponds, according to the spring model, to a doubling of the mass of the hydrogen on substituting H by D.

The formula H—O—O—H for H_2O_2 is accordingly proved. Detectable quantities of $\begin{matrix} \text{H} \\ \diagup \\ \text{O}=\text{O} \\ \diagdown \\ \text{H} \end{matrix}$ cannot be demonstrated in hydrogen peroxide by means of the RAMAN effect. A molecule of the structure H—O—O—H , since substituents make an angle at the oxygen atom, is however able to possess different forms with distinguishable symmetries. Consequently a decision between these various conceivable forms has yet to be made. Of these, three are distinct, namely a mirror-image symmetrical, a centrosymmetrical and an asymmetrical with a perpendicular arrangement of the two OOH planes relative to each other:



Six normal vibrations fall to forms I and III, and only three to form II. If, in addition to these distinct forms, any other particular form with an intermediate arrangement of the OOH planes were present, there would appear in the RAMAN spectrum not sharp lines but broad bands. Since this is not the case, the latter possibility is excluded. Of the three distinct forms, the centrosymmetrical II does not come into consideration for the reason that it does not possess a dipole moment, whereas a moment of about 2.1 D has been found for hydrogen peroxide. The number of lines observed in the RAMAN spectrum corresponds — as will not be established in detail here — to five normal vibrations, that is, only a single form of the molecule can in practice be present. (The sixth normal vibration, the torsional vibration about the O—O axis, escapes observation, since its RAMAN frequency differs too little from that of the exciting line.) An unequivocal

ascription of the observed frequencies to the individual normal vibrations is possible. One arrives thus far with a qualitative interpretation of the RAMAN spectrum. A quantitative evaluation, which cannot be reproduced here ¹¹⁶ — for this, a coupling of the vibrations of the two equivalent O—H bonds and, in consequence, a resonance must be taken into consideration — indicates that the two OOH planes are mutually perpendicular, the molecule thus having the form III. The formula with a single O—O bond is thus in agreement with the RAMAN spectrum as well as with the dipole moment. Nevertheless, at a first glance the conclusions concerning the molecular form appear to contradict one another, since the dipole moment works out at the right value when all the positions of the H atoms about the O—O axis are assumed to be approximately equally abundant (p. 346), whereas the RAMAN spectrum points to the existence of only a single form. This contradiction disappears when it is recalled that the dipole moment has been calculated from measurements on very dilute solutions in dioxan and ether, whereas the RAMAN spectrum has been photographed for pure hydrogen peroxide.

In this connection, the case of hydrazine H_2N-NH_2 will be mentioned for which, by means of the infra-red spectrum ¹¹⁷ in conjunction with the RAMAN spectrum, a completely unsymmetrical configuration has been deduced ¹¹⁸, the two halves of the molecule carrying out torsional vibrations about the N—N bond ¹¹⁹.

8. Magnetic Measurements

(i) Historical and Experimental Background

Magnetic measurements have been employed in the investigation of the states of bonding between atoms only relatively recently. This is due to the fact that, until the time when the chemical bond began to be understood with the help of quantum mechanics, the theoretical relationships between magnetism and state of bonding were almost completely non-apparent. Certainly there was a theory which enabled the phenomena of dia- and paramagnetism to be grasped quantitatively on the basis of the electronic theory, namely the theory of LANGEVIN dating back to the year 1905, but this broke down in some essential points, such as in explaining the magnetic behaviour of substances at very low temperatures; nor could it be related in a satisfactory manner to the state of bonding between atoms.

¹¹⁶ Such is to be found, as also a more exhaustive qualitative discussion than that just given, in the article by A. SIMON, *Z. angew. Chem.*, 1938, **51**, 794.

¹¹⁷ W. FRESSENIUS and J. KARWEIL, *Z. physik. Chem.*, 1939, **B 44**, 1.

¹¹⁸ Quantum-theoretically founded model due to W. G. PENNEY and G. B. B. M. SUTHERLAND, *Trans. Faraday Soc.*, 1934, **30**, 898; *J. Chem. Phys.*, 1934, **2**, 497.

¹¹⁹ J. GOUBEAU, *Z. physik. Chem.*, 1940, **B 45**, 237.

On this account, *magnetochemistry*¹²⁰ had for a long time to limit itself to determining the magnetic constants of substances and trying to bring order on a purely empirical basis into the numerical values found thereby, without being able to enquire into the closer relationships with constitution and atomic structure. In this method, the *magnetic induction* B is measured experimentally in a medium for a known field strength H of the exciting field. Apart from particular exceptional cases, namely the saturation phenomena for ferromagnetic substances, B proved to be proportional to H . The proportionality factor μ in the equation $B = \mu H$ is a constant of matter, the *permeability*, and is characteristic for the medium. For empty space it possesses the value 1. If it is smaller than unity, the substance is diamagnetic, if larger than unity, paramagnetic. If μ is very strongly positive, one then speaks of a ferromagnetic substance. Although the permeability is a quantity which, experimentally, is measured directly, use is not made of it in magnetochemistry, because it still contains the behaviour of a vacuum in the magnetic field. For this reason, a quantity is chosen which gives expression to the difference relative to a vacuum, and therefore pertains purely to matter. This is the *susceptibility* κ , which is connected with the permeability by the relation: $\mu = 1 + 4\pi\kappa$.

Therewith the directly observable permeability appears to be divided into two parts, one belonging to a vacuum and one to the substance. The latter may be negative, namely for diamagnetic substances, and positive in the case of paramagnetic substances.

As a characterizing constant for the substance whose magnetizability is measured, one does not choose, κ which is a quantity referred to the unit of volume, but the *molar susceptibility* $\chi = \frac{\kappa \cdot M}{d}$, referred to the volume of one mole. The numerical values of χ found for different substances have now to be related to the constitutions of the substances in question. Here various rules have resulted for certain classes of substances, whereas for others the values must simply be taken for granted, without being able to accomplish anything with them other than treating them as a measure of the magnetism. Such is the case for metals, for example. On the other hand, relationships with the constitution are to be seen in the χ values found for organic compounds, which are invariably negative. The diamagnetism of these substances was shown by the investigations of PASCAL to be, in first approximation, an additive property¹²¹. By that time, however, the

¹²⁰ W. KLEMM, *Magnetochemie. Physik und Chemie und ihre Anwendungen in Einzeldarstellungen*, Vol. I (Akad. Verlagsges., Leipzig, 1936); S. S. BHATNAGAR and K. N. MATHUR, *Physical Principles and Applications of Magnetochemistry* (London, 1935); E. C. STONER, *Magnetism and Matter* (London, 1934); P. W. SELWOOD, *Magnetochemistry* (Interscience Publishers, New York, 1943); W. KLEMM, *Magnetismus und Konstitution*, *Z. Elektrochem.*, 1945, 51, 14.

¹²¹ More recent measurements are due to W. R. ANGUS and W. K. HILL, *Trans. Faraday Soc.*, 1943, 39, 185; 190; 197. See also S. SUGDEN, *J. Chem. Soc.*, 1943, p. 328.

task of determining the constitution stood very much in the foreground in organic chemistry, and the observation of physical properties had, in essence, the purpose of assisting in this. Consequently one became interested preferentially in those properties which were easy to observe and resulted in simple rules. But because other properties — which in broad outlines could be regarded as additive with certain constitutional peculiarities superimposed upon the additive scheme — were here able to serve better than the molar magnetic susceptibility (the molecular refraction in particular), the extensive investigations of PASCAL did not obtain wide-spread importance. In the field of inorganic chemistry, not much was to be read out of the observational material which gradually piled up, even though special details, like the strong paramagnetism of the salts of the transition metals from chromium to nickel, were striking. The numerical material did not invite more extensive research, because in reality there were no experimental guiding lines.

The position began to change when more precise ideas of atomic structure came to be developed on the basis of BOHR's theory. Soon KOSSEL¹²², in drawing up his theory of heteropolar compounds, pointed to the fact that paramagnetism is characteristic of elements and ions with incomplete electron shells, and, in doing so, even then formulated a magnetic displacement law, the content of which was: *Ions of neighbouring elements containing the same number of electrons are similar in their magnetic behaviour.* Thus, for the first time, even if only empirically, a relationship between magnetism and atomic structure was established.

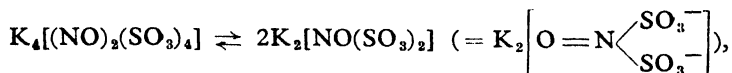
A relation with the molecular structure was discovered by G. N. LEWIS¹²³. He found quite universally that compounds with an odd number of electrons were paramagnetic. Thus NO_2 with 17 valence electrons is paramagnetic, whereas N_2O_4 with 34 valence electrons is diamagnetic. Free radicals in organic chemistry are paramagnetic, their dimers diamagnetic. Still other examples for this rule were found in inorganic chemistry with the compounds NO and ClO_2 . If a compound was observed to be diamagnetic, it could thus not contain an odd number of electrons. This conclusion is especially valuable in the case of ions in solution whose molecular weights cannot be determined directly¹²⁴. The salts of hypophosphoric acid prove themselves to be diamagnetic, that is, they must contain the ion $\text{P}_2\text{O}_6'''$, and the acid salts the ion $\text{H}_2\text{P}_2\text{O}_6''$, but *not* the ions PO_3'' and HPO_3' respectively. Consequently, by reason of the magnetic behaviour of its salts, hypophosphoric acid must be assigned the formula $\text{H}_4\text{P}_2\text{O}_6$. It further became possible to explain the strange behaviour of the so-called FREMY's salt

¹²² W. KOSSEL, *Ann. Physik*, 1916, [iv], **49**, 229.

¹²³ G. N. LEWIS, *Chem. Rev.*, 1924, **1**, 231.

¹²⁴ Certain conclusions may be drawn from the rate of diffusion. Cf. pp. 200, 205.

$K_2[NO(SO_3)_2]$ ¹²⁶ which in the solid state is yellow, in solution deep blue. The solid salt is diamagnetic, the solution paramagnetic. In solution, therefore, a dissociation takes place in the sense of the following equation:



which explains the change in colour.

Such a success achieved in the field of inorganic chemistry by the application of empirical rules naturally provided an attraction to occupy oneself more thoroughly than formerly with magnetochemical investigations. But the real incentive for magnetochemical research came only when, on the basis of the quantum theory, the magnetic properties of matter began to be theoretically understood and, with this, the above-mentioned rules to be grasped.

(ii) The Theory of Magnetism

The theory of magnetism was originally purely physical in nature. It commenced with the observation that an electric current, that is, electricity in motion, generates a magnetic field. Quite soon after this fact became known, the assumption was made by AMPÈRE in 1825 for the explanation of ferromagnetism, that in iron molecular currents flowed without resistance in circles, the magnetic moment of these currents being vertical to the plane of rotation. These molecular currents behave like bar magnets of molecular dimensions which become orientated in a magnetic field. In 1852, WEBER was able on the same basis to make diamagnetism theoretically comprehensible. In diamagnetic substances there are no lasting currents, but resistance-free current tracks are present in which molecular currents induced by an exciting field are able to flow. If, by induction, such a molecular current comes into existence, the track of the current tries to take up a position with the induced moment perpendicular to the lines of force of the exciting field, as does a rotatable conductor in which a current is induced on switching on a magnetic field.

AMPÈRE's theory of paramagnetism, like WEBER's theory of diamagnetism, was qualitative in nature. A quantitative theory of magnetism was only possible after the electronic theory had enabled a more precise conception of the molecular currents to be gained. This was developed by LANGEVIN in 1905. To an electron of charge e moving in a circular orbit of radius r

¹²⁶ Formed by the oxidation of potassium hydroxylamine-disulphonate $K_2[HON(SO_3)_2]$ with lead dioxide: E. FREMY, *Ann. chim. phys.*, 1845, [iii], 15, 459; A. R. HANTZSCH and W. SEMPLE, *Ber.*, 1895, 28, 2744; A. R. HANTZSCH, *ibid.*, 1905, 38, 1043; F. RASCHIG, *Schwefel- und Stickstoffstudien*, p. 150 (1924); H. GEHLEN, *Ber.*, 1933, 66, 292. Magnetic measurements: R. W. ASMUSSEN, *Z. anorg. Chem.*, 1933, 212, 317. FREMY's salt absorbs NO, and can be utilized for the absorption of this substance in gas analysis.

with the angular velocity ω must be assigned a magnetic moment $M = \frac{e\omega r^2}{2}$.

For other forms of orbits, somewhat different formulae apply. In a magnetic field, these moments attempt to become parallel to the lines of force, but thermal motion works against such an orientation. The magnetic moment M of a molecule, which is comprised of the moments M_e for the individual electrons contributing to the magnetism, appears in LANGEVIN'S theory to be linked to the measured molar susceptibility by the equation

$\chi_{\text{mol}} = \frac{NM^2}{3kT}$. This formula of LANGEVIN also remains valid when

the quantum theory is made the basis of the derivation of the relation between χ and M . The advance connected with this theory of LANGEVIN now

appears, among other points, in the fact that the CURIE law $\chi = \frac{C}{T}$ for

the temperature-dependence of paramagnetism — so far known only empirically — follows according to the theory from the interplay of the directional action of the field and the disordering action of the thermal motion, as can be seen from the LANGEVIN formula just quoted. Up to that time, it could have been predicted only qualitatively that diamagnetism must be independent of and paramagnetism dependent on the temperature.

The magnitude of the electric moment arising from the circling motion of the electrons, which is independent of the nature of the substance, must, in LANGEVIN'S theory, be accepted as given by experiment. One could have hoped, with the advances in knowledge of atomic structure, to be able to develop detailed conceptions of the electron orbits which would enable the magnetic moment to be calculated from the model of the atom.

But, before that, it was possible to test by experiment whether paramagnetism really originated from the revolution of electrons. If revolving electrons were the cause, these must possess not only a magnetic moment but also a mechanical moment, even if, on account of the minuteness of the mass of the electron, this could be only very small. Notwithstanding, it should then be possible by rapidly rotating a magnetic body constructed of a ferromagnetic substance — for substances with ordinary paramagnetism, the effect to be expected would be too small to be measured — to cause the originally disordered elementary magnets produced by the electrons moving in orbits to become somewhat ordered, since these would experience a directional force on rotation in consequence of their mechanical moment. If such an ordering occurs, then a magnetic field — if only a very weak one — must be created. As BARNETT¹²⁶ found in 1915, such a field is in fact observed. The field strength H can be measured and, from this and the known mechanical velocity of rotation ω_p , the ratio of the mechanical angular momentum p_r to the magnetic moment be subjected to calculation, for which the equation

¹²⁶ S. J. BARNETT, *Phys. Rev.*, 1915, [ii], 6, 171; 239; *Physik. Z.*, 1934, 35, 203.

$$\frac{p_r}{M} = \frac{H}{\omega_p},$$

which will not be derived here, applies.

The ratio of mechanical angular momentum to magnetic moment can be derived hypothetically from the theory of the electron revolving in an orbit, in which the radius does not need to be known since this, while it is of course determinative for the individual values of p_r and M , is eliminated in calculating the ratio. The result of the experiment is however in quantitative disagreement with the theory by a factor of 2. The effect is only half as large as is calculated from the assumption that the elementary magnets consist of electrons revolving in orbits.

The same result is achieved by other experiments in which a mechanical angular momentum is imparted by remagnetizing a body¹²⁷.

Accordingly, the concept of electrons revolving in orbits, that is, ultimately AMPÈRE's idea of molecular currents, is unable to explain the cause of magnetism, at any event for the ferromagnetic and strongly paramagnetic substances examined — besides the iron-group metals, manganous and gadolinium salts have been investigated.

An explanation was possible only after it was realized that it was not sufficient for a comprehension of the structure of atoms to regard the electron simply as a point-like body endowed with charge and mass. Rather, in order to render justice to the observed phenomena, a power of rotation about an axis must be ascribed to the electron, for which two senses of rotation exist. With respect to the axis of rotation there are thus two possible arrangements for the electron. The angular momentum of an electron, the electronic rotation, is usually called the *spin*. According to the quantum theory, there are only two rotational states for the electron characterized by the quantum numbers $+\frac{1}{2}$ and $-\frac{1}{2}$. The necessity for assuming such a spin for the electron resulted primarily from the splitting of spectral lines, e.g., from the fact that the lines of the alkali-metal atoms are doublets, which is not comprehensible in the absence of an electronic spin (Chapter IV, p. 257 ff).

The electronic spin has the effect of attributing a *magnetic moment*, the *spin moment*, to the *electron itself*. For the occurrence of paramagnetism, it is thus not at all necessary for an electron to move in an orbit. If, for the substances with which the forementioned experiments were made, the electronic spin is assumed to be the cause of the magnetism, then the calculated ratio of mechanical to spin moment agrees with observation.

The possibility that an electron revolving in an orbit gives rise to a magnetic moment still exists in other cases, however. In consequence, paramagnetism can have two distinct causes, that is, it can arise from the orbital

¹²⁷ A. P. CHATTOCK and L. F. BATES, *Phil. Trans. Roy. Soc.*, 1922, **A 223**, 257; W. SUCKSMITH and L. F. BATES, *Proc. Roy. Soc.*, 1923, **A 104**, 499; W. SUCKSMITH, *ibid.*, 1925, **A 108**, 638. This was qualitatively observed by A. EINSTEIN and W. J. DE HAAS.

moment or the spin moment of the electrons. As is seen from experiment, the two possibilities are not mutually exclusive. There are substances in which the spin moment alone or the orbital moment alone causes the magnetism, as well as those in which the two moments are simultaneously operative. In the latter case, the magnitude of the total moment cannot be calculated additively from the orbital moment and spin moment, for the total moment is composed vectorially out of the orbital and spin moments.

The orbital moment and the spin moment cannot assume any desired value, but are related to a quantity, the BOHR magneton μ_0 , according to a relationship governed by quantum numbers. According to the older quantum theory, which assumed electrons revolving in orbits within the atom, the magnetic moment should be integral multiples of the BOHR magneton. In accordance with this older theory, this can be calculated in the following manner from BOHR's model of the atom, in which an electron of mass m and charge e revolves about the nucleus at a distance r and with angular velocity ω :

$$\left. \begin{array}{l} \text{mechanical angular momentum } p = m\omega r^2 \\ \text{magnetic moment } M = \frac{1}{2} e r^2 \omega \end{array} \right\} \text{hence } M = p \frac{e}{2m}$$

According to the quantum theory, the mechanical angular momentum is able to assume only one value, which is equal to or an integral multiple of $\frac{h}{2\pi}$. Consequently the magnetic moment must be equivalent to or an integral multiple of

$$\frac{h}{2\pi} \cdot \frac{e}{2m} = \frac{eh}{4\pi m},$$

that is, of the BOHR magneton μ_0 (see p. 263).

In the newer quantum theory this relation appears in a somewhat changed form, since here the quantum numbers no longer have the readily comprehensible meaning that they have in BOHR's model of the atom. The following relations are valid:

$$\text{orbital moment } M_L = \sqrt{L(L+1)} \cdot \mu_0 \text{ (older theory } L \cdot \mu_0 \text{);}$$

$$\text{spin moment } M_S = 2 \sqrt{S(S+1)} \cdot \mu_0 \text{ (older theory } S \cdot \mu_0 \text{).}$$

The subsidiary quantum number L can run through the sequence of whole numbers from unity upwards, the spin quantum number S integral and half-integral numbers beginning at $\frac{1}{2}$. (When several electrons with parallel spins operate collectively, in deriving the spin moment the individual spin quantum numbers have to be summed to give the quantum numbers S for the total spin.) Thus, in the event that only the spin is determinative, the following M values are obtained when n electrons are present:

number of electrons n	1	2	3	4	5
quantum number S	$\frac{1}{2}$	1	$\frac{3}{2}$	2	$\frac{5}{2}$
M (in BOHR magnetons)	1.73	2.83	3.87	4.90	5.92

The joint operation of orbital moment and spin moment of the electrons in an atom or molecule depends upon which way the individual orbital momenta and spins interact with one another, that is, how they are *coupled*. Two limiting cases may here be distinguished. In the first, which is the more frequent, the orbital angular momenta of the different electrons and the spins of the different electrons are respectively closely coupled among themselves. This is the RUSSEL-SAUNDERS coupling or *LS* coupling. In the second, the so-called *jj* coupling, a strong interaction occurs between the orbital momentum and spin of an individual electron. For such an electron it is then no longer possible to speak of a subsidiary quantum number and a spin quantum number. The interaction between different electrons is then only small. There are also transitions between both types of coupling in which, in addition to a coupling of orbital momenta and spins of different electrons, a coupling of the orbital momentum and spin of an individual electron also occurs.

An *LS* coupling occurs with the electrons of atoms of elements with low atomic numbers and also very frequently in other cases. A *jj* coupling occurs for the orbital momentum and spin of the unpaired electron in nitric oxide NO (p. 394). A not quite pure *LS* coupling exists in the case of the ferromagnetic elements of the iron group.

(iii) Magnetism of Individual Atoms

For a given model of the atom, in which the electronic levels are occupied according to the theory of atomic structure, it is further possible to calculate how the orbital and spin moments arising from the individual electrons in a single atom combine to give a total moment. The atomic moment thus calculated theoretically is capable of a direct experimental testing. In the experiments originated by O. STERN and W. GERLACH, atomic beams were produced and deflected in an inhomogeneous magnetic field (p. 261). These experiments provide the component of the total moment of the atom lying in the direction of the field. In a whole list of cases, outstanding agreement between experiment and theory has resulted. Thus, beams of zinc, cadmium, mercury, lead and tin atoms are not deflected. According to theory, the atoms of these elements do not possess magnetic moments in their ground states. With hydrogen, the alkali metals and silver, as theoretically predicted, the deflection corresponds to an atomic moment of the magnitude of one magneton, with thallium to an atomic moment of $\frac{1}{2}$ magneton. In some cases, in which a pure *LS* coupling does not occur, an exact theoretical calculation is not possible. Individual exceptions exist in which, for still unexplained reasons, experiment and theory do not agree, as in the case of iron, the atoms of which, contrary to expectation, are not deflected. These exceptions cannot alter the fact that the theory of the origin of the magnetic moments of atoms receives the best support from the atomic-beam method.

(iv) Magnetism of Molecules and Crystal Lattices

The testing of the theory of magnetism by the atomic-beam method is particularly valuable, because, with the isolated atom, the question how the valence electrons of an element behave in forming molecules or on entering a lattice is eliminated. One can reckon in the case of ions in a manner similar to that for free atoms, provided it is certain that the investigated substances are heteropolar and their components are really ions. Thus the ions of the alkali and alkaline-earth metals, of the halogens and of many other elements possessing an even number of electrons and no incomplete inner shells are diamagnetic, as are the rare gases with the same electronic configurations. Just as atoms with odd numbers of electrons are paramagnetic, ions with odd numbers of electrons also exhibit the normal paramagnetism, as does the cupric ion Cu^{2+} , for example. It was in this way possible to prove the divalence of silver in the argentic-pyridine-complex, *e.g.*, in the salt $[\text{AgPy}_4]\text{S}_2\text{O}_8$.¹²⁸ The fact that indium dichloride InCl_2 is not paramagnetic but diamagnetic indicates that, as in the like case of HgCl , not simple In^+ and Hg^+ ions but the double ions In_2^{2+} and Hg_2^{2+} occur in the lattice.

If, however, instead of single atoms or ions, molecules are present, then the way in which the valence electrons behave in forming molecules is of great moment. Knowledge concerning the influence of chemical bonding on the magnetic properties enables an investigation of the state of bonding by magnetochemical methods to be carried out. On the formation of *homopolar bonds*, the valence electrons arrange themselves in pairs with their spins antiparallel (p. 403). If all the valence electrons are thus used or remain over in lone pairs, then the compounds are diamagnetic, apart from a vanishingly small number of exceptions which, like the oxygen molecule, demand a special explanation.

If, after the pairing off of electrons in homopolar compounds, an unpaired electron should remain over, the respective compound is paramagnetic (rule due to G. N. LEWIS — see p. 380). The paramagnetism may thereby arise from either the spin moment or the orbital moment of the unpaired electron, or from both.

Should the atoms coalesce not to molecules but to lattices in which the valence electrons still preserve a certain independence, that is, to lattices like those formed by metals and alloys, the relationships are less simple.

In a metal, the electrons may be present together as conducting electrons without marked interaction. They then stipulate a weak paramagnetism, which is sometimes named degenerate paramagnetism¹²⁹. It is temperature-dependent and has the order of magnitude $\chi = +10^{-5}$. Superimposed upon it is the diamagnetism of the metal ions remaining after subtracting the conducting electrons, so that it does not always succeed in making

¹²⁸ W. KLEMM, *Z. angew. Chem.*, 1929, **42**, 396; *Z. anorg. Chem.*, 1931, **201**, 32. Cf. G. T. MORGAN and S. SUGDEN, *Nature*, 1931, **128**, 31.

¹²⁹ Theory: W. PAULI, *Z. Physik*, 1927, **41**, 81.

itself directly apparent. Particularly in the larger atoms, diamagnetism predominates. Degenerate paramagnetism appears almost pure in the metals sodium, magnesium and aluminium, and also still fairly pure in potassium, whereas diamagnetism already preponderates with caesium, and likewise with copper, silver and gold. The carbides and nitrides TiC, TiN and ZrN, which are "metallic" conductors, exhibit degenerate paramagnetism.

In a metal lattice, a strong interaction of the elementary magnets packed closely throughout the lattice frequently takes place. This can have as consequence either that the elementary magnets try to orientate themselves parallel to one another, when *ferromagnetism* occurs: or — and this is more usual — that the effect favours an antiparallel orientation, when the metal exhibits a strong paramagnetism, which one is accustomed to calling *anti-ferromagnetism*. The temperature-dependence of susceptibility in these two cases is other than in ordinary paramagnetism, since, apart from the fact that the orientating action of the external field and the direction-disturbing action of thermal motion work against each other as in ordinary paramagnetism, the temperature-dependent powers of orientation of the elementary magnets in the lattice play an additional rôle. Since a strong interaction between the elementary magnets leading to orientation is necessary for ferromagnetism, it is understandable that this is connected with the crystalline state.

Finally, loosely bound valence electrons which possess a particular relationship with the cores of the atoms are able in certain lattices, as in the case of metallic bismuth, to bring about an anomalously high diamagnetism.

The various possibilities for the magnetic behaviour of substances are collected, together with their temperature-dependences, in the ensuing table.

kind of magnetism	cause	temperature-dependence	κ at $\sim 20^\circ$	examples
diamagnetism	closed shells with spins in antiparallel pairs	none	$\sim -10^{-5}$	rare gases, H ₂ , N ₂ , Hg atom, ions like Cl', SO ₄ '', Na', Ag'
normal paramagnetism	moments of free electrons (orbital or spin moment or both)	$\kappa = \frac{C}{T}$	$\sim +10^{-3}$	H atom, alkali atoms, NO, elements and ions with partly filled shells like Mn ⁺⁺ , Cr ⁺⁺⁺ , rare earths
degenerate paramagnetism	conducting electrons	none	$\sim +10^{-5}$	Na, K, Mg, Al, TiC, TiN, ZrN
ferromagnetism	} exchange forces between atomic moments	$\kappa = \frac{C}{T-\theta}$	$\theta > 0$	Fe, Ni, Co, Gd $< +16^\circ$, Dy $< -168^\circ$ ¹³⁰
antiferromagnetism			$\theta < 0$	Pt, Pd
anomalous diamagnetism	valence electrons in certain lattices	none	$\sim -10^{-4}$	Bi, Sb, γ brass

¹³⁰ F. TROMBE, *Compt. rend.*, 1945, 221, 19.

In the following, only diamagnetism and normal paramagnetism will be discussed. The other types of magnetism will be treated along with the investigation of the states of bonding in alloys.

(v) Diamagnetism of Inorganic Substances

With the help of the quantum theory, a formula can be derived for diamagnetism which presents the diamagnetic susceptibility as a function of the electron distribution about an atom; it contains the mean distance \bar{r} of the electrons from the nucleus:

$$\chi = -2.83 \times 10^{10} \times \Sigma \bar{r}^3.$$

In order to utilize it, an assumption must consequently be made concerning the spatial distribution of the electrons. This can be avoided by working instead with the experimentally found value for the polarizability $\bar{\alpha}$ ¹³¹. In this case the nuclear charge makes an appearance in the formula:

$$\chi = -3.08 \times 10^6 \times \sqrt{Z\bar{\alpha}}.$$

This formula is however only approximately valid, but is found to be in good agreement with experiment.

According to the way in which they are calculated, somewhat different values are obtained for the atomic susceptibilities of rare gases and rare-gas-like ions¹³², which, where they have been compared with experiment, agree satisfactorily. In the case of the rare-gas-like ions, a direct testing is not possible, since, in the salts, cations and anions are always present simultaneously. Here one must consequently be satisfied with an agreement between the sum of the χ values calculated for cation and anion and the value observed for the salt. In this, a correction is further to be applied to the calculation for the uninfluenced ions, since an interaction between the ions in the lattice or in solution arises (which will not be discussed further here). It will only be mentioned that the χ value of a crystalline salt is rather smaller than that in solution, in which a further interaction between the dissolved ions and the water also enters into the picture.

Since the theoretically derived values are reliable, it is possible to use them for comparisons even when the atomic susceptibilities cannot be subjected to observation, as in the case of elements which form molecules. With this it is apparent that the susceptibility of the compound is always smaller than the sum of the atomic susceptibilities. Thus, for the following, for instance, $\underline{\chi} \times 10^6$ is:

¹³¹ J. G. KIRKWOOD, *Physik. Z.*, 1932, **33**, 57; J. P. VINTI, *Phys. Rev.*, 1932, [ii], **41**, 813.

¹³² Diamagnetism of rare-gas-like ions: W. KLEMM, *Z. anorg. Chem.*, 1940, **244**, 377; 1941, **246**, 347; 1942, **250**, 233 (Table with summary).

	H ₂	N ₂	Cl ₂	CO ₂
χ_{atom}	2.37	7.89	22.3	9.12 (C) 6.75 (O)
χ_{molecule}	4.00	12.00	40.4	20.8
Σ_{atom}	4.74	15.78	44.6	22.62

This is also to be expected theoretically, since, in the formation of stable molecules from atoms, the potential energy of the outer electrons becomes lowered. With the consolidation of the electron sheath, the mean distance of the electrons from the nuclei and consequently the dimension of $\Sigma \bar{r}^2$, which is proportional to χ , is reduced. How great this reduction is depends upon the type of bonding. However, it has not yet proved possible to carry out a quantitative calculation which at the same time would provide a relationship with the type of bonding, if only for the reason that the calculation of atomic susceptibilities provides, according to the procedure adopted for the evaluation of $\Sigma \bar{r}^2$, rather different values for χ_{atom} . Consequently the significance of diamagnetism for the investigation of the state of bonding in inorganic molecules has, up to now, been practically nil. In organic molecules the state of affairs is somewhat different, inasmuch as it is here possible from the deviations from additivity of the calculated atomic constants (which are not to be confused with the theoretically derived atomic susceptibilities mentioned previously) to reach conclusions concerning particular types of bonding (p. 379), without the necessity of a detailed understanding of the causes of the deviations from additivity.

(vi) Paramagnetism of Ions and its Relationship with the Paramagnetism of Elements¹³³

Metals with incomplete inner shells, which are pronounced cation builders, are to be found in two places of the Periodic System, namely the *transition elements* from the scandium group to the iron group, and the family of rare earths following lanthanum, the *lanthanides*. The existence of an open shell causes paramagnetism (p. 380), since in such not all the electrons neutralize one another pair-fashion with respect to their orbital and spin moments, which would lead to diamagnetism. For the filling of such shells by electrons there is namely the rule that all possible energy levels in succession must be singly occupied; and only then, when each has been once filled, is one energy level after the other doubly occupied by electrons having antiparallel spins.

¹³³ Compilation of the atomic susceptibilities of paramagnetic metals from Sc to Ni, Y to Pd, La to Pt, Th and U: H. BOMMER, *Z. anorg. Chem.*, 1941, **247**, 249. The highest susceptibilities are possessed by Mn with 530, Pd with 550 and U with 620×10^{-6} .

This is HUND's rule of maximum multiplicity¹³⁴, as — with less lucidity — it is named. A few examples will be given. The M shell is able to contain in its *d* electron subgroup a maximum of 10 electrons. The iron atom possesses 6 electrons in this *d* subgroup. These might mutually neutralize their orbital and spin moments in three pairs, so that a diamagnetic atom resulted. This they do not, however. In preference, 4 of these *d* electrons remain without partners: these are unpaired, and hence contribute to the magnetic moment. By contrast, the fifth is neutralized by the sixth, since the *d* subgroup is half-filled with 5 electrons, so that the sixth on entering must consequently pair off with another. The N shell can take up to a total of 14 electrons in its *f* subgroup, which commences to be filled with cerium. The praseodymium ion Pr⁺⁺⁺ contains 2 electrons in this subgroup which do not pair off, and is thus paramagnetic. In the transition-metal series, the maximum number of unpaired electrons in the *d* subgroup of the M shell is achieved by manganese with 5 electrons. In the rare-earth series, the maximum number of unpaired electrons in the *f* subgroup of the N shell is attained in the case of gadolinium with 7 electrons.

The transition elements and the rare earths are differentiated in the structure of their electron envelopes, in that the former have the M shell with its incomplete *d* subgroup immediately below the outermost shell, whereas, with the rare earths, between the uncompleted N shell and the outermost P shell there still lies the O shell. From these, usually, namely to the extent that the rare earths appear as trivalent elements, one *f* electron together with two *s* electrons belonging to the P shell act as valence electrons. Because, in the case of the rare earths, the uncompleted electron shell is extensively shielded, it makes little difference for the susceptibility whether the ions are present in a crystalline salt or in solution. With the transition elements, on the contrary, the influence of the surroundings — whether their cations are combined with anions in a lattice or in solution — is quite marked.

For the trivalent ions of the rare earths, it is possible to calculate from the quantum numbers, with the assumption of a pure *LS* coupling between orbital momentum and spin, the number of multiples of a magneton μ_0 to which their magnetic moments amount. According to a formula¹³⁵ not to be derived here, from the quantum numbers *L*, *S* and *J* of the ground state, the moment, expressed in magnetons, is found to be

$$M = \sqrt{J(J+1)} \left(1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \right) \mu_0.$$

¹³⁴ This comprises a part of HUND's rules of stability (F. HUND, *Z. Physik.*, 1925, 33, 345). Today they may also be expressed: In the ground state, the spin and orbital moments of the electrons of a subgroup orientate themselves with respect to each other in such a way that the greatest possible spin moment and orbital moment arise.

¹³⁵ Cf., in this connection, A. LANDÉ, *Z. Physik*, 1921, 5, 231; 7, 398; 1923, 15, 189.

Agreement between the values calculated from this and the observed values is in general good, as the following table illustrates (see also Fig. 46):

trivalent ion of	quantum numbers			M in magnetons	
	L	S	J	calculated	observed
La	0	0	0	0	diamagnetic
Ce	3	$\frac{1}{2}$	$\frac{5}{2}$	2.54	2.37— 2.77
Pr	5	1	4	3.58	3.41— 3.60
Nd	6	$\frac{3}{2}$	$\frac{9}{2}$	3.62	3.45— 3.62
Pm	6	2	4	2.68	
Sm	5	$\frac{5}{2}$	$\frac{5}{2}$	0.84	1.32— 1.36
Eu	3	3	0	0	3.12— 3.61
Gd	0	$\frac{7}{2}$	$\frac{7}{2}$	7.94	7.81— 8.2
Tb	3	3	6	9.72	9.0 — 9.8
Dy	5	$\frac{5}{2}$	$\frac{15}{2}$	10.65	10.5 —10.9
Ho	6	2	8	10.61	10.3 —10.5
Er	6	$\frac{3}{2}$	$\frac{15}{2}$	9.60	9.4 — 9.6
Tm	5	1	6	7.56	7.2 — 7.5
Yb	3	$\frac{1}{2}$	$\frac{7}{2}$	4.54	4.4 — 4.6
Lu	0	0	0	0	diamagnetic

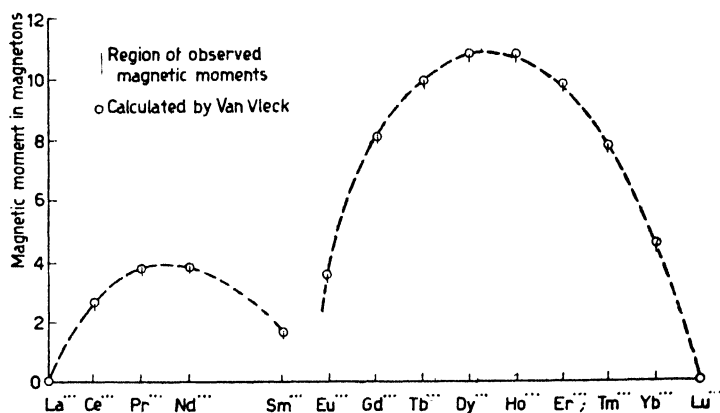


Fig. 46. Magnetic moments of the ions of the rare earths: \circ calculated with pure LS coupling of orbital momentum and spin; | values observed for various compounds.

Noteworthy disagreement occurs only in the cases of samarium and europium. This cannot be attributed to the non-occurrence of a pure LS coupling, for an abnormal temperature-dependence is ascertained for the susceptibilities of the ions of these elements (which does not obey the usual CURIE law), so that a temperature-dependent moment results. The reason for this ¹³⁶ is rather to be sought in the possibility that it is not the moment for the ground-state ion alone which is observed, but that, in addition to this state, on increasing the temperature yet others only slightly richer in energy make an appearance. For the latter states, quantum numbers other

¹³⁶ J. H. VAN VLECK and A. FRANK, *Phys. Rev.*, 1929, [ii], **34**, 1494; 1625.

than those for the ground state pertain, and consequently also other moments.

Most of the elements in the rare-earth group have as metals almost exactly the same susceptibilities as their trivalent ions. This signifies that in the lattices they yield up all their valence electrons as conducting electrons. Their degenerate paramagnetism is negligible in comparison with the paramagnetism of the ionic cores, since it is smaller by about two powers of ten. There are admittedly exceptions to the rule that the trivalent ion and metal possess the same susceptibility, notably in the cases of europium and ytterbium. Europium has about the same susceptibility as the gadolinium ion, while metallic ytterbium is diamagnetic like the succeeding lutecium ion. The N shells of these metals must consequently be filled by electrons to the same extent as those of the trivalent ions of their right-hand neighbours in the Periodic System, corresponding to KOSSEL's displacement law. This is possible if they have given up only two of their valence electrons as conducting electrons in the metal lattice, and allowed the third from the O shell to enter the incomplete *f* electron subgroup of the N shell. This subgroup is thereby completed in the case of ytterbium, and for europium exactly half filled. The elements europium and ytterbium thus form lattices in which they are present as divalent ions with displacement of a single electron from the *d* subgroup of the O shell into the *f* subgroup of the N shell.

This divalency is not surprising, inasmuch as it also occurs in salts precisely in the cases of europium and ytterbium¹³⁷. In addition, samarium is also able to appear as divalent. The special tendency to occur as a divalent element is easily understandable in the case of ytterbium, since in Yb²⁺ the N shell is just filled. The half-filling of the subgroup as occurs in Eu²⁺ and Gd³⁺, as experience also shows in other cases, is likewise especially marked. Thus terbium, which stands on the side of gadolinium opposite to europium, further forms in addition to the trivalent ion a tetravalent ion Tb⁴⁺, the electronic configuration of which corresponds to Gd³⁺. Likewise in the case of the transition elements, a favouring of half-filled subgroups of electrons is recognizable.

Moreover, it is not through the magnetic measurements, which supply a direct proof of the valency, that one has come to assume the presence of divalent ions in metallic europium and ytterbium. The course of the atomic-volume curve¹³⁸ has already indicated the exceptional positions taken up by these two elements, which possess much greater atomic volumes than the remaining rare earths. By contrast, their atomic volumes fit well into a curve which descends from divalent barium (p. 244, Fig. 30).

The transition elements from titanium to zinc are, with the possible

¹³⁷ For example, the colourless YbCl₂: W. KLEMM and W. SCHÜTH, *Z. anorg. Chem.*, 1929, 184, 352.

¹³⁸ W. KLEMM and H. BOMMER, *Z. anorg. Chem.*, 1937, 231, 155. Compilation for all the rare earths: H. BOMMER, *ibid.*, 1939, 242, 279.

exception of titanium¹³⁹, able to form divalent cations in salts, and several of them trivalent cations as well. With the exception of the zinc ion, all of these cations are paramagnetic. The number of BOHR magnetons per ion (see Fig. 47) reaches a maximum of 5.9 with the manganese ion, with which,

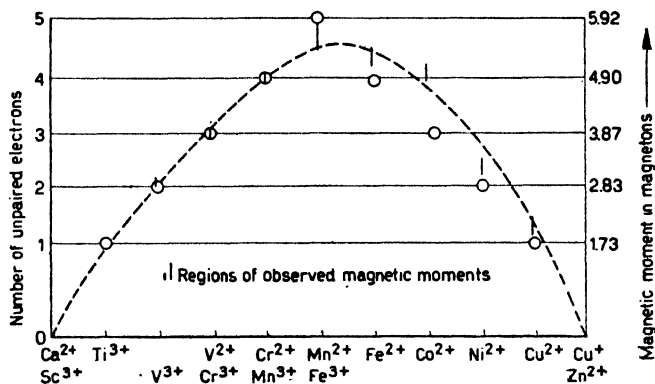


Fig. 47. Magnetic moments of ions of the transition elements: ° calculated with the spin moment only; | values observed for various compounds. It is to be observed that the majority of lines are longer, and that consequently the differences in the observed values are larger than in Fig. 46.

according to KOSSEL's magnetic law of displacement, the ferric ion coincides. V^{••} and Cr^{•••} likewise show agreement in their magneton numbers. With the assumption that only the resultant electron spin determines the magnetic moment according to the formula $M = 2\sqrt{S(S+1)} \cdot \mu_0$, the number of magnetons can be calculated in good approximation with observation. The greatest deviation appears with the cobaltous ion. A calculation which assumes *LS* coupling as for the ions of the rare earths here leads almost entirely to completely wrong figures. Why the orbital moment is here to such a great extent excluded in the formation of a magnetic moment is not quite certain. Apparently the anions present in the solid salt or in solution influence the electrons in the outer incomplete *d* subgroup of the cations in such a way that the orbital magnetic moments appear as largely eliminated. The not inconsiderable influence which the states of combination and solution exert on the magnitude of the moment also supports this¹⁴⁰.

(vii) Paramagnetic Molecules

Oxygen. — The spin alone determines the magnetic moment of oxygen, as in the case of organic radicals with unpaired electrons. The special type of bond in oxygen (p. 407) brings with it the condition that two bonding electrons with parallel spins are here present, their spin quantum

¹³⁹ Compounds of divalent titanium are also known, but are particularly unstable, so that the Ti^{••} ion is not known in aqueous solution.

¹⁴⁰ In this connection, see the theoretical consideration of E. C. STONER, *Phil. Mag.*, 1929, [vii], 8, 250; (for the Co^{••} ion in particular) P. WEISS, *J. phys. radium*, 1930, [vii], 1, 1.

numbers of $\frac{1}{2}$ consequently adding up to 1. According to the formula for the spin moment given on p. 384, the latter thus becomes

$$M_S = 2 \sqrt{S(S+1)} \cdot \mu_0 = \sqrt{8} \cdot \mu_0 = 2.83\mu_0.$$

From this follows for the molar susceptibility according to the LANGEVIN formula (p. 382):

$$\chi_{O_2} = \frac{N\mu_0^2}{3kT} \times 8$$

This value agrees very well with the measured value. The CURIE law is very exactly fulfilled.

Nitric oxide. — In the case of nitric oxide, on the other hand, the CURIE law is not obeyed at all. The number of effective magnetons calculated from the χ values is here not constant, but decreases strongly with decreasing temperature. In spite of the involved situation, a quantitative theoretical explanation has here been successfully given¹⁴¹. Two factors have made this more difficult. One is that, in nitric oxide, instead of the usual single ground state from which the next higher is removed by a considerable amount of energy, there are two states which lie energetically very close to each other. This is to be gathered from its spectrum. The proportion in which the two states are present varies with the temperature. Whereas at very low temperatures, practically only the state which is somewhat poorer in energy occurs, the relative proportion shifts with increasing temperature in favour of that at the somewhat higher energy level, until at higher temperatures both states are practically equally abundant. The second factor is the temperature-dependence of coupling between orbital momentum and spin. At low temperatures the coupling is a strong *jj* coupling, while with increasing temperature an increasing uncoupling takes place. Consequently, at high temperatures the spin can orientate itself independently in a magnetic field.

The two states must first be considered with strong coupling and then with the coupling removed.

With a *jj* coupling, the part of the moment $M_L = L \cdot \mu_0$ arising from the orbital angular momentum, and the part $M_S = 2m_S \cdot \mu_0$ caused by the spin add up, so that

$$M = M_L + M_S = \mu_0(L + 2m_S).$$

The quantum number L of the component of the orbital angular momentum along the line joining the atomic nuclei in N—O here has the value 1. The spin quantum number m_S depends on the mutual configuration of the coupled orbital-momentum component and spin component. In the ground state which is somewhat lower in energy, the two components are antiparallel with respect to each other, that is, $m_S = -\frac{1}{2}$, while in the somewhat energy-richer state they are parallel, with $m_S = +\frac{1}{2}$. The "splitting" of the ground state into two states lying energetically close together thus rests upon the fact that the orbital momentum and spin can be

¹⁴¹ J. H. VAN VLECK, *Electric and Magnetic Susceptibilities*, p. 269 ff.

antiparallel or parallel to one another, which makes little difference for the total energy of the molecule, much less than when, as is usual, an electron must be promoted to a higher energy level in order to arrive at the excited state next above the ground state.

The magnetic moments for the two states are different. For the lower, as results from the insertion of $L = 1$ and $m_S = -\frac{1}{2}$ into the equation, $M = 0$, that is, it is diamagnetic. For the higher, $M = 2\mu_0$, it thus being paramagnetic.

Thus, on retrospectively considering the relative proportion of the two states, it becomes understandable why the susceptibility of nitric oxide should sink rapidly at very low temperatures and tend towards the value 0, while at high temperatures it approaches a value corresponding to two magnetons.

But the temperature curve is not reproduced quantitatively by the temperature-variable equilibrium of the two states of different magnetic behaviour; for, as already mentioned, an uncoupling of orbital momentum and spin also plays a part. In the limiting case of complete uncoupling, the energy-poorer state becomes paramagnetic like the energy-richer. Since, then, the orbital and spin moments orientate themselves completely independently in a field, each corresponding to its effective magneton number, in this limiting case the same moment $M = 2\mu_0$ is attained for both states. Theoretically, when all the factors are considered, the temperature-dependence of χ can be represented by an equation which contains the energy difference ΔE between the two ground states as the only characteristic constant for nitric oxide, this being exactly known from the spectrum:

$$\chi = \frac{N\mu_0^2}{3kT} \cdot Z^2, \text{ in which } Z = 2 \sqrt{\frac{1 - e^{-x} + xe^{-x}}{x + xe^{-x}}} \text{ and } x = \frac{\Delta E}{kT}.$$

The agreement between theory and experiment is outstandingly good, as can be seen from Fig. 48, which reproduces the temperature-dependence of the effective magneton number.

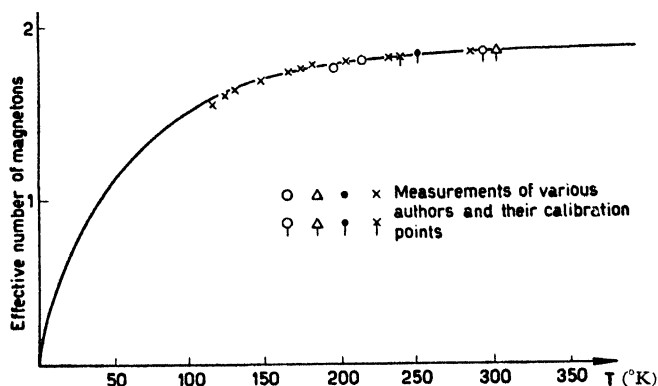


Fig. 48. Effective magneton number for nitric oxide in dependence upon the temperature: calculated and measured values

(viii) Magnetism of Complex Compounds

Elements with an incomplete inner shell immediately under the outermost shell are exceptionally capable of forming stable complexes. The $\text{Fe}(\text{CN})_6^{4-}$, $\text{Ni}(\text{CN})_4^{2-}$, $[\text{Co}(\text{NH}_3)_6]^{3+}$ and PtCl_6^{2-} ions may suffice as examples. But these elements also form less stable complexes like $[\text{Ni}(\text{OH}_2)_6]^{2+}$ and $[\text{Co}(\text{OH}_2)_6]^{3+}$. Although there are transitions, two limiting cases can nevertheless be clearly recognized, and are to be distinguished as *penetration complexes*, which are very stable, and *addition complexes*. As these names suggest, a difference in their spatial content is noticeable. For the groups in addition complexes, the spatial requirement is about the same as in the free state, whereas with the penetration complexes, it is reduced (p. 319). Two distinguishable types of bonding must therefore occur in the two kinds of complexes, in which the possibility that there are transitions between the two naturally does not appear to be excluded. Since, in the complex compounds of the forementioned metals, electrons from the inner shells are able to participate in bonding, in which the kind of activity determines the magnetic behaviour of the compounds of these elements, magnetic investigations are employed to provide information concerning the state of bonding.

In the addition complexes, the nature of the substituent has only a slight influence on the magnetic behaviour of the central atom, for example, on Ni in $[\text{Ni}(\text{OH}_2)_6]^{2+}$ and $[\text{Ni}(\text{NH}_3)_6]^{2+}$. The central atom appears paramagnetic to a degree which also corresponds to its usual behaviour in non-complex compounds. For example, as has already been discussed on p. 393, the magnetic moments for such complexes of the transition elements of the iron group can be calculated with good approximation from the spin of the unpaired electrons in the *d* subgroup.

By contrast, the moment of the paramagnetic central atom is considerably changed in the penetration complexes. Thus potassium ferrocyanide $\text{K}_4[\text{Fe}(\text{CN})_6]$ is diamagnetic, while the central ferrous ion possesses a moment of some 5.2 magnetons. To be sure, potassium ferricyanide is still paramagnetic, but has a moment of only about 2 magnetons, whereas the ferric ion is to be ascribed a moment of over 5 magnetons (5.86 in $\text{Fe}_2(\text{SO}_4)_3$). Among others, the salts $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ and $\text{K}_2[\text{Ni}(\text{CN})_4]$ are also diamagnetic.

If, in attempting to explain this state of affairs, one is content to attribute the paramagnetism of an element in a compound simply to the incompleteness of an inner shell, the diamagnetism of many penetration complexes will be explained by the completion of the shell through the assumption of electrons from the surrounding groups. With such an explanation, which, since it fails to grasp the real nature of the bonding, is essentially formal, SIDGWICK¹⁴² ascribed the diamagnetism and stability of the ferrocyanide

¹⁴² N. V. SIDGWICK, *The Electronic Theory of Valency*, pp. 109 ff, 163 ff, 204 ff (Oxford Univ. Press, 1927).

and hexammine-cobaltic ions to the attainment of the electron number 36 of the rare gas krypton (cf. p. 59).

Fe ²⁺ possesses 24 electrons 6 CN' contribute 12 electrons "effective atomic number" 36	Co ³⁺ possesses 24 electrons 6 NH ₃ contribute 12 electrons "effective atomic number" 36
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With this alone, however, still no comprehensive theory has been given, although in yet other cases the electron number in stable complexes likewise becomes equal to that of a rare gas (p. 58 ff). Indeed, there are also very stable complexes in which it is smaller by 2. Thus, the "effective atomic number" for Ni(CN)₄' is 34, for AuBr₄' 84, and for Pt(NH₃)₂Cl₂ 84 (radon has the atomic number 86).

A deeper insight into the filling up of incomplete shells in the formation of penetration complexes has been gained by PAULING¹⁴³. According to this, the filling of the *d* subgroup by electron pairs originating from the surrounding groups is bound up with a regrouping of the electronic positions. One can imagine this as occurring in such a way, that the electrons present in the incomplete shell of the central ion neutralize one another pair-fashion with respect to their orbital momenta and spins, the remaining unoccupied positions becoming occupied by electrons from the groups. These, together with the *s* and *p* electrons of the groups functioning as bonding electrons, provide similar bonds. These bonds number 6, leading to an octahedral structure if 4 places in the *d* subgroup are vacant; 4 leading to a square planar structure if 2 places in the *d* subgroup are vacant; and 4 leading to a tetrahedral structure if the *d* subgroup is either complete or contains 6 unoccupied places. The following are examples.

Six octahedral bonds: Fe(CN)₆'''', Co(NH₃)₆''' — the central atom has, as ion, 6 electrons in the *d* subgroup which are able to come together as 3 pairs, there remaining two positions to be doubly occupied = places for 4 electrons. (There is room for 10 electrons in the *d* subgroup.)

Four square bonds: Ni(CN)₄' — the central atom has, as the nickel ion, 8 *d* electrons to be grouped in 4 pairs, there remaining one position to be doubly filled = room for 2 electrons; AuBr₄' — the auric ion in the *d* subgroup of the O shell, like the divalent nickel ion in the *d* subgroup of the M shell, has one position doubly vacant when the 8 electrons are collected together in pairs.

Four tetrahedral bonds: Zn(CN)₄'', Cu(CN)₄''' — in the zinc ion the *d* subgroup is complete, as also in the cuprous ion. In all cases, each group contributes 2 electrons to the bonding, as has also been assumed by SIDGWICK.

The kind of bonding in the penetration complexes cannot be further studied in detail by means of magnetic measurements. From these it is only possible to deduce whether or not, in the formation of penetration complexes, all the electrons in the *d* subgroup and, on occasions, other electrons present

¹⁴³ L. C. PAULING, *J. Am. Chem. Soc.*, 1931, **53**, 1367; 3225.

are able to neutralize their orbital momenta and spins in pairs, as in the examples already quoted. Simple addition shows that complete neutralization is not possible in the following complexes, which are consequently paramagnetic:

- $\text{Fe}^{\text{III}}(\text{CN})_6'''$ — there remains a gap in the d subgroup, which hence contains an unpaired electron.
- $\text{Co}^{\text{II}}(\text{CN})_6''''$ — the d subgroup is full. The single electron over and above the number in $\text{Fe}^{\text{II}}(\text{CN})_6''''$ must be raised to a higher level, where it remains as an unpaired electron which is easily given up with the formation of the diamagnetic $\text{Co}^{\text{III}}(\text{CN})_6''''$ complex.
- $\text{Cu}(\text{NH}_3)_4''$ — in Cu'' , the d group still has a gap. In order to make place for the two bonding electrons of an attached group, an electron must be raised to a higher level, where it remains as an unpaired electron.

A theory of penetration complexes entering still further into details is due to VAN VLECK¹⁴⁴. In certain cases it even permits a calculation of the paramagnetism of complexes which are not diamagnetic. A complete calculation of this kind has been accomplished for $\text{K}_3\text{Fe}(\text{CN})_6$ ¹⁴⁵. In this, in addition to the spin moment of the unpaired electron, the orbital moment is also effective, so that its moment of 2 BOHR magnetons is somewhat larger than the value of $1.73 \mu_0$ valid solely for the spin of a single electron.

The additional action of the orbital moment makes it in general difficult to decide, in the case of a paramagnetic complex, whether a penetration complex is under discussion or not, since a calculation of the magnetic moment is not always relatively easy to carry out, as in the case of the ferricyanide ion. If the deviation of the measured magnetism with respect to the value calculated by taking only the spin moment into account turns out to be larger, one may entertain considerable doubts whether indeed one is dealing with a penetration complex. In this connection, W. KLEMM¹⁴⁶ has expressed the suspicion that, in certain complexes, states intermediate between penetration and normal complexes are present, namely in those for which considerable differences exist between the observed magnetism and that calculated from the spin moment alone. An instance of such appears to occur in the complexes of phthalocyanine (p. 329) with divalent manganese, divalent iron¹⁴⁷

¹⁴⁴ J. H. VAN VLECK, *J. Chem. Phys.*, 1935, **3**, 807.

¹⁴⁵ J. B. HOWARD, *J. Chem. Phys.*, 1935, **3**, 813.

¹⁴⁶ H. SENFF and W. KLEMM, *J. prakt. Chem.*, 1939, [ii], **154**, 73.

¹⁴⁷ If this complex adds on pyridine or quinoline, the iron attains the co-ordination number 6 as in $\text{Fe}(\text{CN})_6''''$, and the complex becomes diamagnetic: SENFF and KLEMM, *op. cit.* (footnote 146), p. 79. The situation is exactly the same in the porphyrine-complexes, in which, by the addition of two groups with each bringing one electron pair with it for the bonding, divalent iron attains the co-ordination number 6: L. C. PAULING and C. D. CORYELL, *Proc. Nat. Acad. Sci., U.S.*, 1936, **22**, 159. Many nickel complexes are diamagnetic in the crystalline state and paramagnetic in the dissolved state, which is apparently connected with the transition from a square to a tetrahedral complex. Pyridine is able to convert a square complex into an octahedral. J. B. WILLIS and D. P. MELLOR, *J. Am. Chem. Soc.*, 1947, **69**, 1237.

and perhaps also divalent cobalt, in which the planar structure favours the formation of a penetration complex, although the number of electrons present is not in itself favourable for its formation. Such a transition type also appears to occur in the porphyrine-complexes, as in dicyanoammine-benzene nickel $(\text{NC})_2\text{Ni}\cdot\text{NH}_3\cdot\text{C}_6\text{H}_6$ ¹⁴⁸. In such cases, one may well have arrived at the limit of ability of the magnetic method to determine the state of bonding, until it is possible quantitatively to calculate the influence of the orbital moment from theory, not only for particular cases but quite generally. The magnetic method is of course powerless from the outset where the same magnetism is calculated for the penetration complex as for the normal complex. An example of this occurs with the vanadyl complex of phthalocyanine, which contains the divalent VO group as the central "atom"¹⁴⁹. From the weak paramagnetism, which in both possibilities corresponds to one BOHR magneton, follows only the fact that the vanadium must be tetravalent.

¹⁴⁸ K. A. HOFMANN and F. KÜSPERT, *Z. anorg. Chem.*, 1897, **15**, 204.

¹⁴⁹ P. A. BARRETT, C. E. DENT and R. P. LINSTEAD, *J. Chem. Soc.*, **1936**, p. 1719.

CHAPTER VI

THE CHEMICAL BOND

1. Chemical Bonding between Like Atoms

(i) Hydrogen

Although a knowledge of the electronic configurations of the individual elementary atoms is necessary for understanding the formation of the various chemical bonds, it is however not sufficient for grasping how the chemical bond comes into existence as occurs in the simplest case between two hydrogen atoms. For this, a knowledge of the states which an atom can assume is also required. To describe these, information is necessary concerning the frequency with which the electrons are to be encountered in definite positions relative to the nucleus, and what the energies in the individual positions are. From this, the interactions between the atoms on approaching one another follow in turn, notably whether repulsion or attraction occurs with the formation of a chemical bond. The necessary data are contained in the so-called *eigenfunctions*, which are therefore expressions for the abundance of the electrons in the various positions and the associated energies of the atoms. A complete development of the concept of the eigenfunction and of the SCHRÖDINGER equation upon which it is based cannot be given here, since for this the aid of quantum mechanics is essential, the theoretical-physical and mathematical foundations of which cannot be made comprehensible in a short space. But it is possible to portray, by the example of the eigenfunctions of the hydrogen atom, what information regarding the electron distribution can be inferred from them.

Firstly, one has to reckon with the eigenfunctions of an atom, and not with a single eigenfunction. The mathematical form of an eigenfunction depends upon the quantum numbers, and can thus be different for the ground state and excited states. Included in the eigenfunctions are charge and mass of the nucleus as well as of the electron (or nuclei and electrons respectively for complicated structures), the quantum numbers which fix the state of an atom, and the space co-ordinates which describe the position of the electron, that is, the distance from the nucleus and the angle with the co-ordinate axes selected with the nucleus as origin. The following results for the different quantum states of the hydrogen atom.

For the ground state — principal quantum number $n = 1$, and all the

remaining quantum numbers equal to zero — the eigenfunction is spherically symmetrical. This means that the electron is to be encountered equally frequently in every direction in space, there being consequently no favoured plane, as was the case with BOHR's older model for the hydrogen atom with its electron rotating in an orbit. But the electron is not to be found equally frequently at every distance from the nucleus. Rather, the eigenfunction is of such a form as to show a pronounced accumulation within a certain distance from the nucleus. The distance r from a point which lies in the middle of this small zone of accumulation corresponds in meaning to the radius of the orbit in the old model due to BOHR.

For an excited state, in which the principal quantum number is greater than one but all the other quantum numbers are equal to zero, the spherical symmetry of the eigenfunction remains preserved. For this, consequently, only the distance r at which the electron is most frequently to be encountered is changed relative to the ground state.

Excited states in which the subsidiary quantum number is greater than 0 and in which the magnetic quantum number can also assume a value other than zero no longer possess a spherical symmetry. Owing to the fact that the quantum numbers l and, on occasions, likewise m enter into the eigenfunction, certain directions, as far as concerns the spatial arrangement of the electron, become preferred above the others, so that over an average in time the electron is very frequently to be found in these, but in other directions scarcely ever. Such unsymmetrical eigenfunctions of excited states become of account in the interaction of two neighbouring hydrogen atoms, whereby attraction or repulsion can occur, according to the nature of the eigenfunctions of the two atoms. The bond arising between them, the single bond, will now be examined in detail.

The single bond is effected by an electron pair. The simplest example of this is the hydrogen molecule. How it is that the interaction between two atoms is able to lead to bonding between two atomic nuclei cannot be understood by classical physics. For this, the concepts of the quantum theory are necessary. However, these alone are not sufficient. Certain other assumptions concerning the electron have also to be made, since it does not suffice to represent this simply by a point possessing mass and electrically endowed with the elementary unit of charge. All the same, it is not necessary to go into more precise details concerning the nature of the electron, it sufficing for a comprehension of the chemical bond to ascribe to it the properties of a top capable of rotation. As a mass extended in space and turning about an axis, it can be assigned a *spin*. Since the electron possesses an electric charge, the spin corresponds to a *magnetic moment*. As in the case of a mechanical top, with the electron the spin can have two senses of rotation. Two electrons, as operative in a single bond, can thus have the same or opposed spins, or, as is also customary to say, possess parallel or antiparallel spins. The magnetic properties enable a decision to be made between the two possibilities.

With antiparallel spins a compensation of the magnetic moments occurs, diamagnetism being observed. With parallel spins the magnetic moments do not counteract each other, and paramagnetism is found. Molecules containing only single bonds are always diamagnetic, that is, they have their electrons in pairs with antiparallel spins. The formation of a chemical bond is dependent upon the direction of spin of two electrons. For a single bond, the spins must be antiparallel, so that the two atoms attract one another and participate in a chemical bond. In general, this is also the rule for other kinds of bonds. But cases also occur in which the electrons have a bonding action when their spins are parallel. The paramagnetic oxygen molecule is an example of this. It can thus not be simply the compensation of magnetic moment which, in the case of antiparallel spins, effects the bonding. It can further be calculated theoretically that the energy liberated thereby is only small and is unable to explain the strength of the chemical bond. Consequently the chemical bond cannot be magnetic in nature. It is rather electric in nature, and the significance of the electron spin for the formation of bonds is other than one of mutual compensation. That is, according to the quantum theory there are two possibilities for the electrical interaction between two atomic nuclei and two valence electrons, of which one leads to bonding and the other to repulsion on the approach of the two atoms towards each other. Their interaction can be described by the eigenfunctions reflecting the states of the atoms, two possible total eigenfunctions being obtained thereby, one *symmetric* and the other *antisymmetric*. From these, it is possible to calculate the electron densities between the nuclei, or, in other words, how frequently the electrons are to be encountered in particular positions in space. These electron densities admit of a clear representation, in that they can be reproduced in the manner of isobars whereby positions of equal electron density are joined by curves. The diagrams thus obtained for the electron density with symmetric and antisymmetric eigenfunctions pertaining to two hydrogen atoms in close proximity are reproduced in Fig. 49.

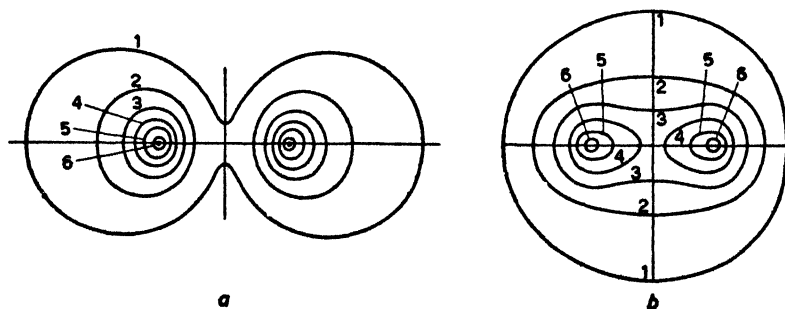


Fig. 49. Curves of equal electron density for two hydrogen atoms in close proximity: (a) antisymmetric total eigenfunction (b) symmetric total eigenfunction

With a symmetric eigenfunction the electrons have a greater probability of being found between the nuclei, whereas the reverse is true with an anti-symmetric eigenfunction. Only in the former case can they effect a bonding action. The possibility of a chemical bond thus exists only when the total eigenfunction is symmetric. Whether now two atoms give a symmetric or antisymmetric eigenfunction depends upon their spins. *The significance of the spin thus exists in effecting a particular form of total eigenfunction.* In the case of two hydrogen atoms, the electron distribution corresponding to the symmetric total eigenfunction, which causes attraction, is produced if the spins of the two atoms are opposed. Hydrogen atoms with the same spin do not attract but repel one another. Briefly summarized, the significance of the spin with respect to the chemical bond exists in governing the density distribution of the valence electrons by determining the form of the total eigenfunction.

As already mentioned, *antiparallel* spins of two electrons usually give rise to a symmetric total eigenfunction and hence chemical bonding. But it also happens on occasions that the total eigenfunction becomes symmetric for *parallel* spins, so that chemical bonding again occurs. In general, it is true, a pair of electrons with parallel spins do not have a bonding action, but an antibonding. For multiple bonds, in the ground states as in possible excited states, these relationships are of importance.

The symmetry of the electron distribution in the hydrogen molecule is a symmetry of rotation about the line joining the two atoms. This also exists for all other single bonds. Bonds with rotational symmetry in their electron densities are termed σ bonds, because this is the kind to which two valence electrons which in the atoms are *s* electrons invariably give rise. They are, however, also possible between *p* electrons, of which point more will be said later. Invariably, only one σ bond can come into existence in one direction.

(ii) Halogens. MULLIKEN's Term Symbols

The bonds in the halogen molecules are likewise single σ bonds of this type. Their formation can be illustrated in two quite different ways. The first manner of representation leads back to the electron-pair bond of the hydrogen molecule, in which, corresponding to the LEWIS-LANGMUIR electron formulae : $\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{F}}}-\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{F}}}$: and : $\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{Cl}}}-\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{Cl}}}$:, the electron pairs are individually considered. In this, the three lone electron pairs on each atom are excluded from consideration as far as the bond is concerned. The justification for this procedure follows from the fact that the same atomic refraction is calculated from the refractive index for chlorine in the chlorine molecule as in organic compounds in which the chlorine is linked to carbon. Hence the activity of the three lone pairs must be independent of the single bond

by which the chlorine is bound. It is consequently possible to say: *in each of the lone electron pairs, the spins of the two electrons mutually compensate one another, and thus exert no combined influence.* There remains only the electron pair between the nuclei, the bonding of which can be treated exactly as in the case of hydrogen.

The second manner of representation treats the electrons of the molecule collectively as an envelope, and distributes them between various energy levels as is usual for the individual atom in BOHR's theory. The heights of these energy levels are compared with the heights of the levels in the individual atom. Electrons which in the molecule must be raised to a higher level are antibonding, those that remain on the same level bonding. For the halogens, this manner of viewing the situation appears much more complicated than the first. For other molecules, however, it is more convenient and more exhaustive. For comparison, it will be illustrated here first for the example of the fluorine molecule.

But first it is necessary to acquaint oneself with the symbolism which is employed in the representation of electronic configurations in molecules. This originated with R. MULLIKEN, who developed this approach. In this, he commenced with the molecular spectra, which, however, need not be further considered here¹.

MULLIKEN numbers the shells known in the theory of BOHR as K, L, M, . . . in sequence as 1, 2, 3, . . . The electrons are subdivided according to the subgroups into *s*, *p*, *d* and *f* electrons. The number of electrons in a subgroup is attached (in a not exactly fortunate manner) as a superscript to the letter signifying the electron type. Thus, by way of examples, a hydrogen atom in the ground state has the configuration $1s^1$ = one electron in the K (1) shell; a nitrogen atom has the configuration $1s^2 2s^2 2p^3$, that is, two *s* electrons in the K (1) shell and two *s* electrons and three *p* electrons in the L (2) shell. For molecules, in which two nuclei have moved up close to one another, the same shells are assumed as for the atoms. The possibilities of occupying the individual shells and the subgroups present in them are thereby the same as for the atom in the BOHR theory. Thus a molecule can have at most two *s* electrons in the K shell, at most two *s* and six *p* electrons in the L shell and at most two *s*, six *p* and ten *d* electrons in the M shell. The principles followed in the derivation of these numbers are the same as in BOHR's theory of the atom. The numbers result from the possible quantum numbers and the PAULI principle, according to which no state may be doubly occupied. In the formation of molecules, interaction occurs between the electrons originating from the individual atoms, which are thereby

¹ The underlying theory was evolved almost simultaneously by R. S. MULLIKEN and by F. HUND. The most important articles are: F. HUND, *Z. Phys.*, 1928, **51**, 859; 1930, **63**, 719; *Handbuch der Physik* (GEIGER and SCHEEL), Vol. XXIV, Part I, p. 561 (1933); R. S. MULLIKEN, *Phys. Rev.*, 1928, [ii], **32**, 186; 1929, **33**, 730; 1932, **40**, 55; **41**, 49; 751; 1933, **43**, 279; *Rev. Modern Phys.*, 1932, **4**, 1; *J. Chem. Phys.*, 1933, **1**, 492; 1935, **3**, 375; 506; 514; 517; 564; 573; 586; 635; 720. See also G. HERZBERG, *Z. Physik*, 1929, **57**, 601.

able to give σ , π and δ bonds. In σ bonding, as already mentioned, the charge distribution has a symmetry of rotation about the line joining the two atoms. This is not the case for π and δ bonding. (π and δ bonds are differentiated by a different dependence of the eigenfunctions on the angle about the line joining the atoms.) s electrons are able to give only σ bonds or, as is also said, assume σ electron states. Of the six p electrons, the maximum number possible in a shell, the first two effect a σ bond, the remainder π bonds. Of the maximum number of ten d electrons, two in turn enter into σ bonding, four into π bonding and four into δ bonding. Instead of "bonding", one would in general more correctly employ the term "interaction", since, in the event that a promotion to a higher level should be necessary, the relevant electrons are not bonding but antibonding.

σ interactions are then such that result in a rotational symmetry of distribution for the respective electrons, π and δ interactions such as for which the electron density is a function of the angle about the line joining the atoms. The possibilities to be distinguished here in the number of operations of the electrons in the electron groups can be briefly collected together in a table which reflects the maximum number of electrons in each subgroup and the nature of their operations:

kind of electron	maximum number	symbol	kind of operation (electron state)	maximum number	symbol
s	2	s^2	σ	2 σ	σ^2
p	6	p^6	σ, π	2 $\sigma, 4 \pi$	σ^2, π^4
d	10	d^{10}	σ, π, δ	2 $\sigma, 4 \pi, 4 \delta$	$\sigma^2, \pi^4, \delta^4$

From this scheme, the operation of the electrons in the molecule² can be formally derived in a *qualitative* way. For all atoms with the exceptions of hydrogen and helium a simplification is thereby possible, inasmuch as the two innermost electrons to be found in the K shell no longer need to be counted up with the others, since they mutually neutralize their spins, do not contribute to the bonding, and are also only very slightly influenced by the kind of operations of the electrons in the more remote shells, indeed, even of those in the L shell³.

We are now at the point where the bonding in the fluorine molecule can be described by specifying the electronic configuration by means of MULLIKEN's symbolism. For the sake of simplicity, the K shell will remain out of consideration. With the configuration $1s^2 2s^2 2p^5$, the fluorine *atom* has

² Named "molecular orbitals" by MULLIKEN, recalling the "electron orbits" in the atom according to the older theory of atomic structure due to BOHR.

³ The magnitude of this extremely small influence follows from the dependence of the frequencies of the K_α and K_β lines in the X-ray spectra on the state of combination. Such small differences are to be found in the case of sulphur as an element and in the sulphates.

two s and five p electrons in the L shell. On fusing together two fluorine atoms to form the fluorine *molecule*, a dinuclear structure arises which, with respect to the levels, is comparable with a mononuclear structure bearing the same total nuclear charge. Since fluorine has a nuclear charge of 9, the atom to be compared with the fluorine molecule possesses the atomic number 18, namely that of argon. The latter has, in its two outermost L and M shells, the following electron levels occupied: two s and six p electron levels in the L shell, and likewise two s and six p in the M shell. The two fluorine atoms bring with them a total of four s and ten p electrons for the L shell. Of the four s electrons, only two can be accommodated in the L shell with the occupation of the σ state. The maximum number of electrons in this shell being thereby achieved, two s electrons must be promoted to the M level and accordingly exert an antibonding influence. Of the ten p electrons, two in the σ state and four in the π state can remain as bonding electrons in the L shell. The remaining four p electrons must be raised to the M level, where they can be housed as antibonding electrons in the π state. Hence, there is a total of four bonding electrons in the σ state, two antibonding in the σ state, four bonding in the π state and four antibonding in the π state. Thus, if one now again includes the K shells and differentiates the individual levels by the letters z , y , x , w and v , the fluorine molecule is ascribed the electronic configuration $KKz\sigma^2y\sigma^2x\sigma^2w\pi^4v\pi^4$. If it is assumed that the bonding and antibonding electrons neutralize one another in their effect, then two electrons in a σ bond remain over. This is the same result as obtained above by other methods.

The counteraction of the effects of the bonding and antibonding electrons to be found in the same state of operation need not be complete. But if it is, as has been assumed here for the sake of simplicity, then the remaining σ bond is uninfluenced by them and can be treated exactly like the σ bond in the hydrogen molecule.

To what extent the actions of the bonding and antibonding electrons in the same state of bonding neutralize each other does not follow from the formal treatment of MULLIKEN. MULLIKEN therefore satisfies himself by arranging the various electronic states in his configurational formulae in order of increasing energy, in which the assignments of energy are denoted by letters counting backwards from the end of the alphabet. If the configurational formula of F_2 is considered from this standpoint, the action of the $z\sigma^2$ electrons is bonding, $y\sigma^2$ antibonding, $x\sigma^2$ bonding, $w\pi^4$ bonding and $v\pi^4$ antibonding.

(iii) Oxygen

How advantageous MULLIKEN'S approach is for gaining an insight into the bonding relationships is shown by the example of the oxygen molecule. From the number of electrons, the octet rule and the fact that only one σ

bond can exist in one direction, it follows that, for 2×6 valence electrons, the link between the two oxygen atoms is effected by four electrons which are to be accommodated in one σ and one π bond. Each atom contains in addition two lone electron pairs: $\ddot{\text{O}}:\ddot{\text{O}}$. Through the use of the electronic

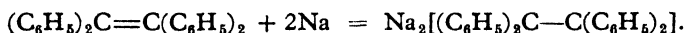
terms, more is learnt concerning the state of bonding. Oxygen has the electronic configuration $1s^2 2s^2 2p^4$. In its number of electrons and nuclear charge, the oxygen molecule corresponds to the sulphur atom, which has accommodated two s and six p electrons in the L shell and two s and four p in the M shell. Omitting the electrons in the K shell, there results for the four s and eight p electrons to be accommodated from the two oxygen atoms room for two s electrons as σ electrons in the L shell (bonding), two s electrons as σ electrons in the M shell (antibonding), two p electrons as σ electrons in the L shell (bonding), four p electrons as π electrons in the L shell (bonding) and two p electrons as π electrons in the M shell (antibonding). The π subgroup in the M shell is incompletely filled. The configurational formula for O_2 thus becomes $\text{KK}z\sigma^2 y\sigma^2 x\sigma^2 w\pi^4 v\pi^2$.

This approach can be still further simplified, if from the outset not only the electrons in the K shell but also the two s electrons in the L shell of each atom are left out of consideration, and only the four in the higher $2p$ level of each oxygen atom are regarded to be active as valence electrons. One is then concerned with only eight valence electrons which, since the L shells have used up their places for s electrons, are to be housed as follows: two σ and four π electrons in the six p positions of the L shell, and two π electrons in the M shell. These constitute three bonding pairs and one antibonding pair of electrons. Thus there results altogether, if the effect of the bonding and antibonding pairs is regarded as (approximately) equal in magnitude, a "double bond" consisting of four electrons, two σ electrons (σ bond) plus two π electrons (π bond).

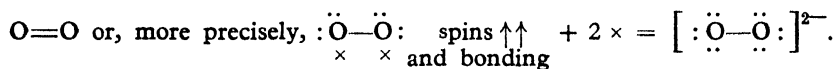
The incompletely occupied π subgroup allows of two possibilities for the kind of bond. The spins of two electrons can be either parallel or antiparallel. In a completely filled group the electron spins must be paired off, that is, antiparallel. This is not necessarily the case for an incompletely filled group. Therefore, according to this qualitative consideration, the π -electron bond in the oxygen molecule may contain π electrons with either parallel or antiparallel spins. Which of the two possibilities is realized can be decided only by virtue of a detailed calculation, in which an excited state with energy differing only little from that of lowest energy, the ground state, must also be considered. This calculation results in parallel spins for the bonding π electrons, which opposes the rule that is usually valid. The paramagnetism of the oxygen molecule is thereby explained. At the same time, it teaches us a difference relative to the double bond between two carbon atoms, which indeed also consists of one σ plus one π bond, but in which the latter contains bonding electrons with their spins antiparallel.

(iv) Peroxide Ions

In addition to the O_2 molecule, oxygen can also form the singly and doubly charged anions O_2' and O_2'' , which are present in the lattices of saltlike peroxides like KO_2 and Na_2O_2 . They originate from the oxygen molecule by the assumption of one or two electrons in the interaction with strongly electropositive metals. Neither of the two ions still contains the double bond of the oxygen molecule. The formation and structure of the O_2'' ion is very easy to understand. The assumption of two electrons is analogous to that which occurs when certain unsaturated compounds are converted to saturated by the action of alkali metals. Ordinary $C=C$ double bonds as in ethylene are admittedly not capable of this, but become so when suitable substituents are present. Thus, for example, tetraphenylethylene can add on sodium:



The $C=C$ double bond also reacts in a similar way. In the case of the oxygen molecule, the π bond, on the assumption of two electrons, is dissolved with the formation of two lone electron pairs, the spins of which are internally neutralized through antiparallel orientation, while the σ bond remains preserved. By the assumption of two electrons, the oxygen molecule attains the same number of electrons as the fluorine molecule. The state of bonding in the O_2'' ion is therefore directly comparable with that in F_2 :



The mode of viewing peroxide-formation, as effected by the assumption of electrons from alkali metals with the preservation of the σ bond of the oxygen molecule in the way depicted here, appears at first sight not to agree with the technical manner of preparing sodium peroxide, since sodium oxide is here originally formed above 180° , this being oxidized to the peroxide only at higher temperatures ($300-400^\circ$). It thus appears as if Na_2O is the primary product. Against this, it is possible to raise the objection that the liquid sodium at the surface undergoing oxidation is always present in a much greater concentration than the gaseous oxygen. Consequently, if Na_2O_2 is formed as the primary product, it must be immediately reduced by the metal to Na_2O . The observation that in the technical process one first obtains Na_2O is thus no proof against the primary formation of Na_2O_2 . A valuable criterion in favour of the original product of the reaction between an alkali metal and oxygen being the peroxide is provided in the formation of potassium peroxide K_2O_2 by the action of oxygen on a solution of potassium in liquid ammonia at -50° ⁴, these being the same conditions under which it has been possible to ascertain the assumption

⁴ Rb and Cs react similarly, and, as has recently been determined, so does Na: W. H. SCHECHTER, H. H. SISLER and J. KLEINBERG, *J. Am. Chem. Soc.*, 1948, **70**, 267.

of electrons by C=C double bonds reactive towards alkali metals⁵ (to which that of ethylene does not belong — see previously). The formation of Na₂O₂ from Na₂O + O₂ at 400° and of BaO₂ from BaO + O₂ at 500°, in which no metal participates, must naturally be brought about in some other way.

The singly charged O₂' ion occurs in peroxides which are formed as stable end products from the oxidation of potassium, rubidium and caesium with molecular oxygen. They are strongly coloured compounds, KO₂ being orange-red and CsO₂ brownish red. Sodium forms a corresponding peroxide under pressure⁶. In addition, KO₂ as well as K₂O₂ can be obtained from oxygen and potassium in liquid ammonia. The structure of the O₂' ion is not so easy to understand as that of O₂'', since no analogy for it exists. The peroxides KO₂, RbO₂ and CsO₂ are paramagnetic⁷. The cause of their paramagnetism cannot, however, be the same as in the oxygen molecule, since it could not be theoretically understood how, with *preservation of the character of the bond*, the internally saturated oxygen molecule should be able to assume a further electron. The results of X-ray structure analysis of KO₂⁸, which forms the same lattice as does calcium carbide, are in agreement with this theoretical requirement. X-ray analysis has resulted in 1.28 Å for the distance between the two oxygen atoms in the O₂' ion and 1.31 Å⁹ for the O₂'' ion in BaO₂, which likewise forms a calcium carbide lattice, the difference between the values for the two ions thus scarcely exceeding the limits of error. In contrast to this, the distance between the atoms in the oxygen molecule is only 1.20 Å. From this it is certain that the state of bonding in the O₂' ion is other than in O₂, and apparently similar in nature to that in the O₂'' ion, that is, a σ bond. The paramagnetism is to be attributed to the unpaired electron. The structure of the O₂' ion is perhaps most conveniently derived from a polar form of the oxygen molecule in which the π electrons are not equally distributed in a π bond between the atoms, but are to be found as a lone electron pair on one of the two oxygen atoms. Such a state is naturally much richer in energy than the ground state

⁵ Cf. W. HÜCKEL, *Theoretische Grundlagen der organischen Chemie*, Vol. I, p. 493 (6th Ed., 1949).

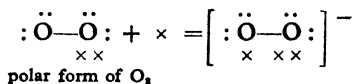
⁶ Preparation of NaO₂ from Na₂O₂ + O₂ under pressure: S. E. STEPHANOU, W. H. SCHECHTER, W. J. ARGERSINGER (JR) and J. KLEINBERG, *J. Am. Chem. Soc.*, 1949, **71**, 1819. Whether analogous peroxides of the alkaline-earth metals, CaO₄ and BaO₄, exist, may, judging from reports so far available, be doubted. In any event, they have not been isolated as pure compounds. The darkening of the colour of the compound BaO₂.H₂O₂ on exposure to light does not permit even a moderately certain conclusion that a new peroxide which might be held responsible for this exists.

⁷ E. W. NEUMAN, *J. Chem. Phys.*, 1934, **2**, 31. The paramagnetism alone, however, is no proof against the formula K₂O₄: W. KLEMM and H. SODOMANN, *Z. anorg. Chem.*, 1935, **225**, 273.

⁸ V. KASATOCHKIN and V. P. KOTOV, *J. Chem. Phys.*, 1936, **4**, 458; *J. Tech. Phys. (U.S.S.R.)*, 1937, **7**, 1468. The formerly much-used formula K₂O₄ is also excluded by X-ray analysis: A. HELMS, *Z. angew. Chem.*, 1938, **51**, 498; A. HELMS and W. KLEMM, *Z. anorg. Chem.*, 1939, **241**, 97.

⁹ J. D. BERNAL, E. D'YATLOVA, I. KASARNOVSKII, S. I. RAIKHSTEIN and A. G. WARD, *Z. Krist.*, 1935, **92**, 344. The lattice is a tetragonal, deformed rock-salt lattice, in which the chloride ions are replaced by peroxide O—O' ions lying in the direction of the fourfold axis (cf. Chapter VIII, 2, (iii)).

of the oxygen molecule with a π bond, and will occur only rarely. The dissymmetry of charge inherent in it can now be partly compensated through the assumption of an electron by the oxygen atom, which has a deficiency of electrons:



If yet a second electron is taken up, the O_2'' ion results. How far the assumption of electrons proceeds is, to all appearances, bound up with the lattice which the peroxide is able to form, and is thus not simply a question of electronic configuration. In this connection, it is worth mentioning that a special stability exists for the lattice type MO_2 with a cationic radius of 1.3 Å or more, irrespective of whether the ion is singly or doubly charged; so that, for the alkali metals, the peroxides with the O_2' ion, and for the alkaline-earth metals, those with the O_2'' ion are stable. Calcium, whose radius is about 1 Å, is able under special conditions to form the peroxide CaO_2 ; sodium, with a radius somewhat smaller still, was for a long time thought incapable of forming a peroxide of the MO_2 type.

(v) Nitrogen

In the case of the nitrogen molecule, not only the electrons of the K shells, but, for the sake of simplicity, also the two s electrons of the L shells will for the moment be left on one side in distributing the valence electrons among the various kinds of functions. Since the electronic configuration of nitrogen is $1s^2 2s^2 2p^3$, for the two N atoms, only six valence electrons come into consideration, all of which can be accommodated in the six p positions of the L shell, two as σ and four as π electrons. They are all bonding. If the remaining electrons are also considered, there results for the configuration of the N_2 molecule: $|\text{KK}|z\sigma^2 y\sigma^2|x\sigma^2 w\pi^4$. The electrons situated between two vertical lines compensate one another (approximately) in their effect. Three electron pairs are thus operative in one σ and two π bonds, so that it is possible to speak of a triple bond, in which (like the electrons in the K shells) the s electrons in the L shells are regarded as inoperative with respect to the bonding. This triple bond, which can be represented by the symbol $:\text{N}\equiv\text{N}:$ — the lone pairs of electrons are the s electrons which have just been mentioned — appears to correspond to the triple bond between two carbon atoms, as it occurs in acetylene. To be sure, the chemical behaviour of the unreactive nitrogen is quite different from that of the extremely reactive acetylene and its derivatives. How far a difference exists here, and how far it is not possible to regard the $\text{N}\equiv\text{N}$ triple bond as directly analogous to a $\text{C}\equiv\text{C}$ triple bond — in the way in which the $\text{O}=\text{O}$ double bond is also not exactly the same as a $\text{C}=\text{C}$ double bond — will be discussed later, when the transference to compounds of bond types obtained for the elements comes up for discussion (p. 421).

2. Bonding between Unlike Atoms

(i) The Single Bond. Bonding to Hydrogen

The hydrogen atom, since its valence electron is an s electron, can be bound only by a σ bond. Its bond with the halogen atoms in the hydrogen halides can be thought of as coming into existence in the same way as the σ bonds in the halogen molecules. The valence electrons of the halogen mutually satisfy one another pair-fashion by antiparallel orientation of their spins, so that only one remains over to be placed at the disposal of the bond with the hydrogen. It is invariably possible to reckon as simply as this when one has to deal with atoms which, as in the case of the halogens, lack only one electron for the completion of an electron group. These behave almost as if only one electron were present in the group. The symmetry of the charge distribution is not so high in the hydrogen halides as in the hydrogen molecule. Nevertheless, the characteristic symmetry of rotation about the line joining the atoms exists for the σ bond, but in the direction of this joining-line there is no longer any symmetry, the bonding electrons being drawn over towards the halogen. To be sure, this does not occur to anything like the extent where one could speak, even with approximation, of heteropolar structures for the hydrogen halide molecules. As follows from the dimensions of the molecules, the hydrogen nucleus is found inside the electron cloud common to both atoms. The electrons are drawn over towards the halogen most strongly in the case of hydrogen fluoride, and least in the case of hydrogen iodide. This fact determines the trend of the dipole moment, which decreases with increasing atomic weight of the halogen. The internuclear distance H—X, which increases in the same order, thus plays only a subordinate rôle in determining the magnitude of the dipole moment. This is illustrated by the following table:

hydrogen halide	HF	HCl	HBr	HI
internuclear distance (Å)	0.92	1.28	1.41	1.6
dipole moment $\times 10^{18}$	1.91	1.03	0.78	0.36

If the hydrogen halides had a structure which even approached the heteropolar, then, since the dipole moment is equal to the product of charge and distance, an increasing moment would necessarily be observed with increasing internuclear distance. The opposite is however the case. Nevertheless, for many purposes it can be useful to picture their formation as the result of the approach of a proton and halide anion. It must then be remarked, however, that the proton approaches so close to the halide ion as to be drawn into the electron cloud of the latter, and that this cloud is increasingly strongly deformed in the sequence F, Cl, Br, I.

(ii) Hydrides of Groups V and VI

For the bonding of hydrogen to polyvalent elements of the fifth and sixth groups, the p valence electrons of these elements are utilized. From the p

eigenfunctions of polyvalent elements with p electrons, it can be derived quite generally that, in combining with a number of monovalent atoms having s valence electrons, a maximum of three σ bonds formed from one p and one s electron respectively are possible in space, the three bonds not all being able to lie in one and the same plane. The derivation of this cannot be given here¹⁰. If these three σ bonds do not reciprocally influence one another, and if also the monovalent atoms exert no forces on one another, then their directions must all be perpendicular to each other. In actual fact, however, this is not the case. In particular, the repulsive forces between the hydrogen atoms (or other monovalent atoms or groups of atoms) act in such a way as to increase the angle to a value above 90° . Consequently the molecules of the hydrides of the divalent elements in group VI, in which only two bonds are present, have the form of an obtuse-angled triangle, and those of the trivalent elements in group V the form of a flattened pyramid with the element at the apex (cf. also later under the halides). The dimensions and angles as well as the dipole moments of the hydrides of groups V and VI are reproduced in the following table:

hydride form	H ₂ O	H ₂ S	NH ₃	PH ₃	AsH ₃
X—H distance (Å)	1.01		1.02	1.46	1.56
distance between the H atoms (Å) } angle	1.53		1.68		
dipole moment (D)	1.84	0.93	1.46	0.55	0.15

The angles are uncertain by several degrees.

The dipole moments decrease with increasing atomic weight of the atom combined with the hydrogen. The cause is the same as in the series of hydrogen halides; namely, the dissymmetry of charge of the X—H bond in the direction of the bond decreases with increasing atomic weight of X in consequence of increasing polarizability of its electron cloud. The measured angles show unequivocally that a spreading of the valencies, which would bring about the same effect, is not the cause (cf. p. 344).

The hydrides of group VI have lone electron pairs. One of these belongs to the s and the other to the p group of valence electrons. The hydrides of group V possess one lone electron pair. These are the two s electrons which, as in the free atom, mutually satisfy one another by an antiparallel configuration of their spins.

(iii) Hydrides of Group IV. The C—H Bond

The elements of the fourth group possess only two p valence electrons. They are however usually tetravalent, and can bind four monovalent atoms or groups by single bonds. Consequently four σ bonds can radiate from them, not only three, as results for the forementioned elements on operating their

¹⁰ Such is to be found in A. EUCKEN's *Lehrbuch der chemischen Physik*, Vol. I, p. 381 (2nd Ed., 1938).

p electrons. The reason for this is to be sought in the fact that, in addition to the two p electrons, the two s electrons may also be operated as valence electrons, although in the isolated atom they have paired off their spins in the antiparallel configuration. This is possible because they do not differ too greatly in energy from the two p electrons. Consequently, in perturbations of the atom, such as occur when it enters into combination with other atoms, they also become involved. One speaks of the two s electrons as being with the p electrons nearly degenerate. By degeneracy is universally understood the phenomenon in which two different states have the same energy. When two electrons in different states have exactly the same energy, they are completely degenerate. If the energy difference is small, they are nearly degenerate. Electrons differing little in energy, as well as those which are completely degenerate, must all be treated in precisely the same manner in a mathematical treatment, and thus it comes about that carbon and the remaining elements of group IV are tetravalent, although in the ground state they contain two not quite equally firmly bound groups of two electrons each in the outermost shell. In the atom operating all its valencies, after the two s electrons which in the ground state had their spins paired off have become uncoupled, all four electrons have attained equality. This requires only a small * expenditure of energy in the case of carbon. In order to bring out the difference between the four electrons in operation and the s and p electrons in the ground state of the atom, the former are denoted as q electrons. Of these, each can enter into a σ bond with the s electron of a hydrogen atom. Since there is an equality between each of the four electrons, the four σ bonds must also be equally distributed in space, and this is accomplished by arranging the four atoms at the corners of a regular tetrahedron with the carbon atom at its centre — the well-known model of the methane molecule.

Methane which has been robbed of a hydrogen atom, the methyl radical

CH_3 , or, more precisely, $\times \text{C} \begin{array}{l} \diagup \text{H} \\ \text{---} \text{H} \\ \diagdown \text{H} \end{array}$, can with its single q electron be treated

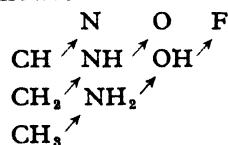
like a hydrogen atom as far as its bonding is concerned, or, in consideration of the total number of electrons, like a halogen atom. If two methyl groups join up to give ethane $\text{H}_3\text{C}-\text{CH}_3$, a C—C bond then comes into existence, which is a σ bond. On account of its rotational symmetry, as far as concerns this bond alone, all the conceivable positions of the two halves of the molecule relative to each other are equally justified. There is thus free rotation of the two methyl groups about their joining-line. A certain restriction of

* *Translator's note.* — There is experimental evidence (cf. L. H. LONG and R. G. W. NORRISH, *Proc. Roy. Soc.*, 1946, A 187, 337; L. H. LONG, *Z. Electrochem.*, 1950, 54, 77) that the energy required to promote a carbon atom to its valence state is in fact as high as about 65 kcal. Theoretical calculations have placed it still higher (cf. J. H. VAN VLECK, *J. Chem. Phys.*, 1934, 2, 20; 297; R. S. MULLIKEN, *ibid.*, p. 782; H. H. VOGEL, *ibid.*, 1936, 4, 581).

this free rotation however comes about in consequence of the forces which the hydrogen atoms exert on each other. The result is that a particular position is favoured, so that with a rotation certain resistances must be overcome. These are however not so large — a few kcal per mol — that, on replacing the hydrogen by substituents, rotational isomers stable beyond the duration of experiment can be isolated¹¹.

(iv) The Hydride Displacement Law

The situation arises where, in the volatile hydrides with homopolar bonding of the hydrogen, the hydrogen nucleus is included in the electron cloud. This makes it possible, in compounds derived from these hydrides by the replacement of one H atom, to treat the remaining group as though it were an atom having a nuclear charge higher than that of the atom which it contains linked to the hydrogen, and that by a number corresponding to the number of H atoms included in the group. This group can thus be regarded as a pseudo-atom, which is thereby imitated¹². Thus, for instance, the hydroxyl group imitates the fluorine atom, whereby it becomes intelligible why, for example, OH and F can replace one another isomorphously in silicates. CH₂ is comparable with O, and CH with N. This similarity can be briefly summarized as follows:



In making comparisons, it must not be forgotten that the hydrogen-containing groups taking the place of elementary atoms do not possess the symmetry of the elementary atoms which they imitate: for example, OH is a decided dipole. With respect to the hydrocarbon radicals, it must be remembered that the 2s electrons are drawn upon to participate in the bonding, these not needing to be touched in the elementary atoms N, O and F.

The compounds H₂O₂ = HO—OH, N₂H₄ = H₂N—NH₂ and hydroxylamine H₂N—OH are comparable to fluorine in the character of their O—O, N—N and N—O bonds. However, on account of the lone electron pairs and the hydrogen atoms, they differ from it altogether in their reactions.

(v) Halogen Compounds

In homopolar bonding, halogens can in first approximation be treated like hydrogen according to the rule that atoms or groups of atoms, in which only one electron is lacking for the completion of a group, behave almost as if they possessed only one valence electron. That this is permissible in the

¹¹ Concerning this, see W. HÜCKEL's *Theoretische Grundlagen der organischen Chemie*, Vol. II, pp. 89 ff and 124 (5th Ed., 1948); cf. also Vol. I, pp. 49—50 (6th Ed., 1949).

¹² W. HÜCKEL, *Z. Elektrochem.*, 1921, **27**, 305; H. G. GRIMM, *ibid.*, 1925, **31**, 474.

compounds the halogens form among themselves in which they function as monovalent elements, namely in ClF and ICl^{13} , needs no further justification. Nevertheless, the functional interaction of this single electron in a σ bond with the remaining electrons may not be neglected completely. Particularly in the bonding of halogens to elements of the higher periods in which the outer shells are not completely filled, like the M shell in the case of silicon, for example, it appears to be possible that, in consequence of the incomplete nature of these shells, the lone electron pairs on the halogens also become involved. That the incompleteness of these shells plays a part in compound-formation by the elements of the second period onwards, follows from the existence of halides in which these elements act as central atoms in their highest states of valency, like, to quote examples, phosphorus in PF_5 and sulphur in SF_6 . Here, in addition to the p electrons, the two s electrons must also function. Further, in addition to the s and p subgroups in the common electron shell of the compound, the d subgroup of electrons, which is not occupied in the free element, must also be partly filled. An older hypothesis, which also wanted to preserve the octet rule for these compounds, and therefore assumed that they contained in part one-electron bonds (singlet bonds), has proved to be incorrect. The octet rule just does not apply here (p. 56). The halogen atoms are everywhere bound by electron pairs in σ bonds. That these σ bonds are however not exactly the same as in the halogen molecules or the hydrogen halides follows from the fact that the interatomic distances in the SF_6 molecule, for example, cannot even approximately be calculated additively from the atomic radii as derived from the interatomic distances in F_2 , H_2 , HF and H_2S , and also from the fact that the calculation of interatomic distances from ionic radii breaks down, as the following summary concerning the hexafluorides of sulphur, selenium and tellurium shows:

	SF_6	SeF_6	TeF_6
observed interatomic distance (Å) ¹⁴	1.57	1.68	1.83
calculated from atomic radii (Å)	1.68	1.81	2.01

In the case of SiCl_4 or SiF_4 , an additive calculation of this sort is likewise not possible, whereas it agrees very well for CCl_4 . From this, it follows that the σ bonds between halogens and elements which do not belong to the first period cannot be comprehended simply according to a scheme, but, for an understanding of their strengths and lengths, demand a calculation embracing all the valence electrons.

For the trihalides of the elements of group V, in which the two s electrons do not visibly take part in the bonding and remain independent as lone electron pairs with saturated spins, the same holds in principle as does for the

¹³ BrCl is not yet known in the pure state.

¹⁴ Mean values from the observations of (a) H. BRAUNE and S. KNOKE, *Z. physik. Chem.*, 1933, B 21, 297 and (b) L. O. BROCKWAY and L. C. PAULING, *Proc. Nat. Acad. Sci., U.S.*, 1933, 19, 68. SF_6 (a) 1.56, (b) 1.58; SeF_6 (a) 1.67, (b) 1.70; TeF_6 (a) 1.82, (b) 1.84 Å.

corresponding hydrogen compounds. The σ bonds form angles amounting to rather more than 90° with one another, the molecules being flat pyramids and possessing dipole moments (see the table on p. 412). The moment given for nitrogen trifluoride NF_3 , namely 0.24 D, is by all means remarkably small, being thus within the limits of error practically equal to 0. In any case, this is not attributable to an almost planar structure, for, according to electron-diffraction experiments¹⁵, the NF_3 molecule is pyramidal with symmetry C_{3v} , and the following dimensions: FNF angle $102.5 \pm 1.5^\circ$; N—F distance $1.37 \pm 0.02 \text{ \AA}$ ¹⁶. The trihalides of group VII, ClF_3 , BrF_3 and ICl_3 , which have not yet been more closely investigated in this respect, will be included here. By contrast, the halides of boron behave in a fundamentally different manner. They possess no lone pair of electrons, but have rather the two s electrons of the boron functioning in σ bonds along with its p electron. With boron, as has already been done in the example of methane, the s and p electrons, as almost degenerate, are to be treated similarly — as also in the case of the halides of group IV. In consequence of this degeneracy, three σ bonds can be formed *in one plane*, these making an angle of 120° with each other. In point of fact, all the trihalides of boron are planar in structure and have no dipoles.

The tetrahalides of the elements of group IV have regular-tetrahedral structures for the same reason as methane, and do not possess dipole moments. What the position is for the tetrahalides of elements from other groups, which in addition to the valence electrons operated in the bonds, also possess other inoperative electrons in the outer shell of the central atom, has not so far been treated from the standpoint of theory, nor investigated experimentally. In this are concerned the compounds SF_4 (SCl_4 is too unstable to be precisely investigated), SeF_4 , SeCl_4 and TeBr_4 . TeCl_4 is certainly not tetrahedral¹⁷, and possesses a dipole moment of 2.6 D in benzene¹⁸. VCl_4 is tetrahedral (Chapter VII, 3, (iii)).

The halides of oxygen in which the halogen is monovalent should, like water, possess the form of an obtuse-angled triangle. And this also applies for the two compounds F_2O and Cl_2O , an angle of about 100° having been determined by electron diffraction for F_2O , and 115° for Cl_2O . Neither Br_2O nor SCl_2 , which must likewise be thought of as belonging to this group of compounds, is known in the pure state. Whether theoretically

¹⁵ V. SCHOMAKER, quoted by S. H. BAUER, *J. Am. Chem. Soc.*, 1947, **69**, 3104. Infra-red spectrum: C. R. BAILEY, J. B. HALE and J. W. THOMPSON, *J. Chem. Phys.*, 1937, **5**, 275.

¹⁶ That PI_3 should have no dipole moment certainly rests on an experimental error, since, according to electron-diffraction experiments, the molecule forms a flat pyramid of about the same dimensions as AsI_3 , for which a moment of about 1 D has been found. The X-ray analysis of crystalline PI_3 (H. BRAEKKEN, *Kgl. Norske Videnskab. Selskabs Forh.*, 1933, **5**, 202) does not permit a decision as to whether the PI_3 molecule is planar or a flat pyramid in the lattice.

¹⁷ Electron diffraction: D. P. STEVENSON and V. SCHOMAKER, *J. Am. Chem. Soc.*, 1940, **62**, 1267.

¹⁸ K. A. JENSEN, *Z. anorg. Chem.*, 1943, **250**, 247.

TeCl_2 and TeBr_2 can be treated like H_2O or Cl_2O is perhaps doubtful. Experimentally it is known concerning the structure of these two compounds which boil above 300° (TeCl_2 324° , TeBr_2 339°) that they are either linear or nearly so¹⁹ (p. 131).

By contrast, with respect to the dihalides of the group-II element mercury a linear structure Cl—Hg—Cl has been determined with certainty for the chloride molecule, both from electron diffraction and from the absence of a dipole moment. This is found again in the lattices of HgCl_2 , HgBr_2 and the yellow modification of HgI_2 . HgF_2 , which first boils in the neighbourhood of 650° and is possibly approaching heteropolar, has not been investigated. So far, the case of the mercury halides has not been treated theoretically. It is worthy of note that lone electron pairs, whose presence stipulate the bent structure of the homopolar oxides X_2O , are not present here. It thus appears as if the possibility of a linear structure results here from the absence of electrons in the outer shell that are not operated, just as does the possibility of a planar structure in the case of the boron trihalides

The special case of those trihalides of the elements in group III which form double molecules at temperatures which are not too high, like Al_2Cl_6 and Ga_2Cl_6 , with which Fe_2Cl_6 is also associated, is very similar to that of diborane B_2H_6 , and, since the formation of double molecules demands quite another approach from that adopted here for compounds of the first order, receives treatment in another place (p. 166 ff).

3. The Double Bond

The type of bond produced on the formation of the oxygen molecule can be designated as a double bond, since the oxygen atoms are linked to one another by one σ and one π bond. However, the concept of the double bond was not introduced for the instance of O_2 , but for the sake of organic compounds, of which the simplest example is ethylene. If one now compares both "kinds" of double bonds, the classical in organic compounds and that in the oxygen molecule, it is impossible to avoid the conclusion that, in spite of the analogy to be expected between CH_2 and O according to the hydride displacement law, far-reaching differences exist. These are apparent in the chemical behaviour as well as in the more detailed theoretical description of the state of bonding. The considerable powers of addition of the $\text{C}=\text{C}$ double bond is found to only a modest extent in the oxygen molecule. To be sure, between the doubly bound carbon atoms one σ bond and one π bond are also present, as in the case of oxygen, but the π electrons bind in a different manner. Whereas in the case of oxygen they have parallel spins, their spins in the carbon link are antiparallel²⁰. As a consequence,

¹⁹ W. GREYHER, *Ann. Physik*, 1936, [v], 26, 1. But cf. p. 131, footnote 91.

²⁰ Concerning this, see W. HÜCKEL's *Theoretische Grundlagen der organischen Chemie*, Vol. II, p. 352 ff (5th Ed., 1948).

ethylene, in contrast to the paramagnetic oxygen, is *diamagnetic*. For ethylene also there is by all means a state, namely an energy-richer excited state, in which the π electrons have parallel spins²⁰, but they are here antibonding in effect, as is usual for pairs of electrons with parallel spins, and not bonding, as in the exceptional case of oxygen. It is therefore not particularly appropriate simply to associate, under the concept of the double bond, the oxygen type of bond with the double bond effected by carbon. Moreover, the oxygen molecule, with its peculiar kind of bonding, stands in a class of its own, while the carbon-carbon double bond has perfect analogues in the N=N double bond of the azo-compounds, in the $>C=O$ double bond of the carbonyls, in the $>C=N$ double bond of the imines and in the $-N=O$ double bond of the nitroso group. In all of these true double bonds, a strong σ bond is present next to a weaker π bond of π electrons with anti-parallel spins, the latter bond determining the reactivity.

This kind of double bond, as met with in organic chemistry, is formed only between elements of the first period. At most it makes an additional appearance between carbon and sulphur in the thioaldehydes and thioketones. Nevertheless, these differ in their properties in part so extensively from their oxygen analogues, that it is possible to doubt whether the kind of bonding in $C=S$ is the same as that in $C=O$. The possibility of a $C=S$ double bond has not yet received a theoretical treatment. This is however the only case where, from the experimental standpoint, the participation of an element of the second period in a double bond appears to be so much as possible. Unsaturated silicon hydrides like $H_2Si=SiH_2$ are unknown. In addition, four-electron bonds between silicon and oxygen, phosphorus and oxygen, sulphur and oxygen, etc., as well as apparently between carbon and phosphorus and between sulphur and nitrogen, do not occur. A theoretical explanation of this has not so far been given.

The difference between the unique double bond which exists in the oxygen molecule and the double bond in ethylene, since in each case one pair of σ electrons and one pair of π electrons are operative in the bond itself, must lie in the different kinds of interaction of these pairs with the remaining electrons. The latter are in ethylene so firmly bound in the four C—H bonds as σ electrons, that they are practically excluded from interaction. For the peculiarity of the $O=O$ bond a certain participation of the not directly operated $2s$ and $2p$ electrons, which are usually written as lone pairs, must therefore be held responsible for the bonding in consequence of reciprocal influencing. And further, it is essential that this interaction originates from *both* atoms, for, when it is eliminated only unilaterally, as in the carbonyl group on the side of the carbon atom with its two single σ bonds, an ordinary double bond occurs, which, like that in $\begin{matrix} H_3C \\ H_3C \end{matrix} \rangle C=O$, is diamagnetic and possesses additive powers.

4. The Triple Bond. Isosterism

The triple bond with which one is familiar in organic chemistry and the triple bond which has to be assumed for the nitrogen molecule differ so extensively from one another, that, as with the double bond in organic compounds and in the oxygen molecule, one may doubt whether they can be appropriately described as the same kind of bonds. The cause of the difference is to be sought in the same direction as in the case of the C=C and O=O double bonds. In order that the well-known strength and inertness of the $\sigma\pi\pi$ triple bond in the nitrogen molecule should come about, the possibility of an interaction between the actual bonding electrons, which were originally p electrons, and the lone pairs of electrons or $2s$ electrons must exist, so that in N_2 one accordingly has really to include all the 10 valence electrons in the bonding system.

The typical representative of a compound with a triple bond, as it is known in organic chemistry, is acetylene. The triple bond between the carbon atoms stipulates a great reactivity, which expresses itself in a tendency towards explosive decomposition and in a readiness to enter into addition reactions. The latter is also found among the nitriles, which contain the triple bond $-C\equiv N$, although the thermal instability is lacking here.

The triple bond of the nitrogen type, which is linked with the presence of a total of ten available valence electrons, is to be found in the following molecules and ions: N_2 , CO^{21} , NO^+ , CN^- , C_2^{--} .

Such molecules and ions, which with the same total number of electrons and nuclear charges possess the same (or at least a very similar) type of bond, are named *isosteric* after I. LANGMUIR. This *isosterism* is not found only in the nitrogen type of compound. There are also other isosteric molecules, such as CO_2 and N_2O (p. 429). It brings about a great similarity in the physical properties, since with isosteric compounds the exterior effect of the electron envelopes, above all to be recognized in the forces of cohesion, is practically the same. It provides the explanation for the already long-known great similarity between the physical properties of nitrogen and carbon monoxide:

	m.p.	b.p.	T_c	p (atm)	v *	$\mu \times 10^{18}$
N_2	-210°	-195.84°	-147°	33.5	0.0040	0
CO	-203°	-191.58°	-140.2°	34.5	0.0042	0.15

* Referred to the volume of 1 g of the gas at 0° and 760 mm as unit.

The molecular spectra are also very similar. The similarity of the electronic configuration is thus effective not only in the ground state, but also in those excited states which determine the emission of the spectra. The effective

²¹ Cf. footnote 28, p. 423.

cross-sections, which result from the scattering of slow electrons as a function of the electron velocity (measured in electron-volts, cf. p. 355), yield in the cases of nitrogen and carbon monoxide, very similar effective-cross-section curves (Fig. 50), since the trend of these curves is governed by

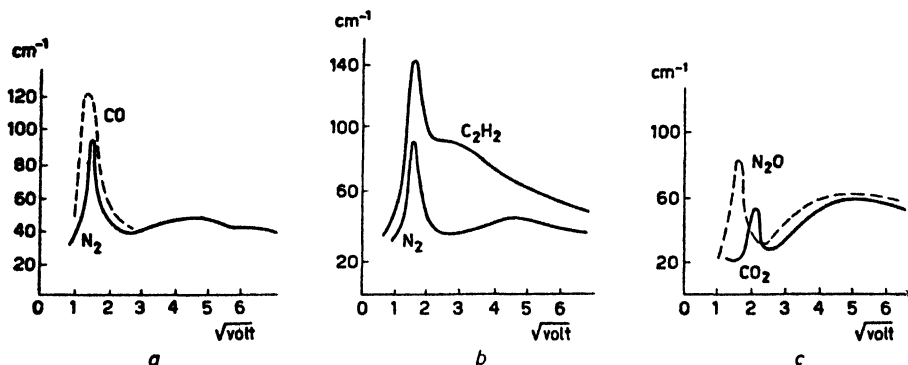


Fig. 50 (a), (b), (c). Effective cross-sections in dependence upon the velocity of the slow electrons scattered. As abscissa, the square root of the velocity expressed in electron-volts has been chosen; as ordinate, the effective cross-section referred to the number of molecules to be found in 1 cm³ at 0° and a pressure of 1 mm of Hg (*i.e.*, 3.54×10^{16}) — that is, a really arbitrarily chosen unit. The effective radius of a molecule in Å can be calculated from the formula:

$$r = 0.30 \sqrt{\text{effective cross-section.}}$$

the outer electrons. Other isosteric molecules like CO₂ and N₂O also resemble one another in the shape of their effective-cross-section curves. The difference between the curves for nitrogen and acetylene is somewhat larger than for N₂ and CO, but here also a certain similarity is unmistakable.

The *nitrosyl cation* NO⁺ is present in the saltlike nitrosyl perchlorate [NO]ClO₄, and is also to be assumed in nitrosyl sulphuric acid [NO]HSO₄²². Likewise the crystalline sublimable “molecular compounds” formed between nitrosyl fluoride and the pentafluorides of arsenic and antimony²³ will be formulated [NO]AsF₅ and [NO]SbF₅ correspondingly. The difficulties encountered in the analysis point to the formation of a stable AsF₅’ complex. For the analogous compound (NO)₂SnCl₆, which is isomorphous with (NH₄)₂SnCl₆, and [NO]BF₄, isomorphous with NH₄BF₄, the crystal structures have been determined²⁴, from which a radius of 1.40 Å is calculated for the nitrosyl cation, that is, just about as large as that of the ammonium ion (Chapter VIII, 4, (i)). The fact that the *cyanide ion* CN⁻ has the electronic configuration of N₂²⁵ explains why the saltlike cyanides do not occur in

²² W. HIEBER AND F. SEEL, *Z. anorg. Chem.*, 1942, **249**, 308; F. SEEL, *ibid.*, 1943, **252**, 24.

²³ O. RUFF, K. STÄUBER AND H. GRAF, *Z. anorg. Chem.*, 1908, **58**, 325.

²⁴ L. J. KLINCKENBERG, *Rec. trav. chim. Pays-Bas*, 1937, **56**, 749.

²⁵ The similarity of the electron envelopes of N₂ and CN⁻ was first pointed out by W. KOSSEL: *Ann. Physik*, 1916, [iv], **49**, 362, footnote 3. Isosterism of N₂, CO, CN⁻ and C₂H₂: W. HÜCKEL, *Z. Elektrochem.*, 1921, **27**, 305.

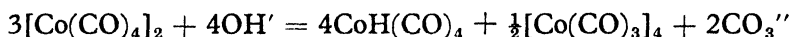
isomeric forms like the organic cyanides, in which either — in the case of the nitriles — a single bond proceeds from the carbon, or — in the case of the isonitriles — from the nitrogen, whereby the symmetry of the electronic configuration is disturbed. For the same reason, the distance between the carbon and nitrogen in the cyanide ion (1.06 \AA^{26}) is appreciably smaller than in the nitriles (mesomerism, cf. p. 432).

The *acetylide ion* C_2'' occurs in the saltlike carbides of the alkali and alkaline-earth metals, of which Na_2C_2 , K_2C_2 , CaC_2 , SrC_2 and BaC_2 are known. In spite of their close relationship with acetylene, which they evolve in the reaction with water, in contrast to acetylene and also more especially to the acetylides of copper and silver, Cu_2C_2 and Ag_2C_2 , they are not explosive. Indeed, calcium carbide is a compound which is even exothermic to the extent of about 15 kcal. One may therefore doubt whether in them the same state of bonding predominates as in acetylene and the heavy-metal acetylides, although X-ray analysis of calcium carbide indicates a close spatial relationship between two C atoms. However, this stability of the saltlike acetylides becomes immediately comprehensible when one thinks of the isosterism of the unperturbed acetylide ion C_2'' with N_2 . In addition to the electrons operated in the $\sigma\pi\pi$ triple bond, the $2s$ electrons of the C or N respectively are still available here, which, although they do not participate directly in the bonding, nevertheless stabilize the bond by interaction with the true bonding electrons. If this interaction ceases through these s electrons becoming fixed by forming σ bonds with hydrogen, then the great stability of the triple bond, whose two σ and four π electrons are henceforth left to their own resources, is at an end. This loss of interaction also sets in when, as in the lattices of the acetylides of copper and silver, a pure ionic relationship between the lattice particles is no longer extant, but the acetylide ion deformed on both sides by the metal ions, two of its electron pairs being claimed for the setting up of a kind of heteropolar bonding. It accordingly appears appropriate to write the formulae of these acetylides like that for acetylene $H-C\equiv C-H$, namely $Cu-C\equiv C-Cu$ and $Ag-C\equiv C-Ag$, but those of the saltlike acetylides, by contrast, according to the manner for complex formulae as, for example, $Na_2[C_2]$ and $Ca[C_2]$ or, in greater detail, $Ca[:C\equiv C:]$. In the formula for the acetylide ion $[:C\equiv C:]^{2-}$, the similarity of its structure with that of the nitrogen molecule receives expression, the latter being also best written not merely with a triple bond, but $:N\equiv N:$ to take account of its $2s$ electrons.

If in a bond of the nitrogen type only one of the two pairs of s electrons is engaged in a σ bond, the triple bond does indeed suffer a considerable loss in stability, but does not develop such a labile condition as in acetylene. Thus, the monosodium derivative of acetylene, $Na[:C\equiv C-H]$, which is employed in syntheses, is reactive but not explosive. The nitriles $R-C\equiv N$ certainly add on easily at the $C\equiv N$ bond and exhibit a tendency towards

²⁶ H. J. VERWEEL and J. M. BIJVOET, *Z. Krist.*, 1938, 100, 201.

polymerization reactions, but are otherwise stable. Further, in heavy-metal cyano-complexes, the cyanide ion is under certain circumstances able to combine by means of the *s* electron pair on the carbon with the heavy metal in really stable bonding, in which this electron pair is included in the electron envelope of the heavy metal. In this, stable shells are frequently formed (p. 396 ff). Similarly carbon monoxide with its pair of *s* electrons on the carbon is, in the metal carbonyls, able to link to the metal atom, whereby, taken together with the electrons of the latter, a stable shell likewise arises. Here, an increased reactivity of the carbon monoxide is sometimes to be noted as, for example, when cobalt tetracarbonyl on being hydrolyzed with strong alkali allows a part of the carbon monoxide to be oxidized to carbonate:



(cf. Chapter VII, 7, (ii)).

Carbon monoxide still requires a special discussion. Its formation from carbon and oxygen, according to the conception which one now has of the state of bonding prevailing in it, can be given a very simple representation, in which one states that the two *p* electrons of the carbon and the four *p* electrons of the oxygen form one σ and two π bonds between the C and O. In this, therefore, the 2*s* electrons on the C as well as on the O are left out of the picture, the carbon atom accordingly formally manifesting itself as in actual fact divalent, which corresponds to the earlier way of representing the carbon in carbon monoxide as divalent. But, on closer examination, this divalence is something quite other than what is otherwise understood by divalence; for the partner of the carbon, namely the oxygen, does not, as in the case when other divalent elements link up with it, take up two electrons or, as in Cl_2O , place two of its electrons at the disposal of the bonds with the other element, but contributes all four of its *p* electrons to the common bond. A triple $\sigma\pi\pi$ bond²⁷ between C and O thereby comes into existence, and not a double bond, which would have to be written: $:\text{C}::\ddot{\text{O}}:$. This triple bond between C and O is also no "ordinary" triple bond, $\text{C}\equiv\text{O}$, but also demands the interaction of the *s* electrons which, in the derivation of the bond type, were previously neglected, so that as a consequence it must be written $:\text{C}\equiv\text{O}:$. Even this manner of writing it is not entirely satisfying, for it reflects a symmetrical distribution of the electrons about the two nuclei, which is indeed present in nitrogen but not carbon monoxide. This follows from the fact that, with symmetrical electron distribution, carbon monoxide would have to possess a considerable dipole moment on account of the different nuclear charges of C and O. But such does not exist. The carbon monoxide molecule actually possesses a just detectable moment of 0.15 D. The oxygen atom, by virtue of its higher nuclear charge, thus draws the electrons over towards itself to such an extent, that its excess of positive

²⁷ But see footnote 28, p. 423.

charge relative to the carbon thereby becomes practically completely compensated²⁸.

In *nitric oxide* NO, whose cation NO⁺ is isosteric with carbon monoxide, the state of affairs is similar to that in carbon monoxide. Here also, holding fast to the constant divalence of oxygen, the nitrogen was formerly spoken of as divalent. Transferring this conception to the electronic theory of valence, NO would have to be written as the radical of the nitroso group, $\overset{\cdot\cdot}{\underset{\times}{\text{N}}}\text{:}\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{O}}}$, with an unpaired electron (\times). With this radical nature, however, neither its relative inertness towards many compounds (not towards oxygen) nor its lack of colour — monomolecular nitroso compounds are blue or green — is in harmony. Furthermore, the distance between N and O is with 1.15 Å equal in magnitude to that between C and O in CO and significantly smaller than that in the nitroso group NO with 1.22 Å²⁹. The quantum-mechanical theory of chemical bonding makes a state of bonding corresponding to one of the above formulae appear completely impossible for the ground state. One can convince oneself of this most rapidly with the help of MULLIKEN'S considerations concerning the occupation of electron groups, in which, for the sake of simplicity, the electrons of the K shell and the 2s electrons of the L shell can be left out. Altogether there are seven *p* electrons available in the L shell, three from the nitrogen and four from the oxygen. Of these, as in the case of the nitrogen molecule, six can be housed as bonding electrons in the L shell common to the molecule as a whole, two in one σ and four in two π bonds. There is no further room for the seventh *p* electron in this shell, which must therefore be raised to the M level and is consequently antibonding in effect. On considering in addition the electrons not directly participating in the bond, the electronic configuration of NO becomes KKz²o²y²o²x²w²v²π⁴vπ. The bond between N and O is thus, like that between C and O, a $\sigma\pi\pi$ triple bond, but weakened by the unpaired electron. The corresponding formula would be : N $\overset{\times}{\equiv}$ O : (\times antibonding). To be sure, this is in contradiction with the octet theory, inasmuch as nine electrons are ascribed to the oxygen. This contradiction is however not irresolvable as soon as one proceeds from NO⁺ and raises the question why this cation, which is isosteric with the nitrogen molecule, should be able to take up a further electron. For a symmetrical distribution of the electrons about the nuclei, the NO⁺ ion, on account of the nuclear charge of the oxygen which is higher by one, possesses a surplus of one positive charge on the oxygen. The positive charge of the ion can thus be thought of as localized on the oxygen. This charge is now compensated in the NO molecule by the unpaired electron, and that so completely that the dipole moment of NO with 0.13 D lies hard on the limits of the measurable. In other words, with a symmetrical distribu-

²⁸ L. H. LONG and A. D. WALSH (*Trans. Faraday Soc.*, 1947, **43**, 342) also speak against an ordinary triple bond in carbon monoxide. See also translator's note, p. 436.

²⁹ F. ROGOWSKI, *Z. Elektrochem.*, 1941, **47**, 152.

tion of the bonding σ and π electrons in the NO^+ molecule, an average of one electron less is thus allocated to the oxygen atom than corresponds to compensation of its nuclear charge ($\text{N}_{5+} \text{O}_{5+}$), the NO molecule possessing this electron more. The special reactions of NO are to be attributed to this electron, as also its paramagnetism. The latter exhibits a peculiarity, in that its magnitude is determined by the orbital moment of this electron as well as by its spin moment — normally the electron spin alone is decisive for the magnitude of the paramagnetism. Experimentally this state of affairs makes itself noticeable in a peculiar temperature-dependence, in consequence of which the CURIE law is not fulfilled at all. The abnormal temperature-dependence finds its explanation in the different influence of the temperature on the orbital and spin moments³⁰ (Chapter V, pp. 394—395).

5. Mesomerism³¹

It can be seen from a comparison of the states of bonding in simple inorganic molecules and in organic compounds, that a simple schematic classification of bond types as in organic chemistry is not feasible in inorganic chemistry. In the examples thus far considered, the difference in behaviour of bond types which are formally equivalent — double and triple bonds — in inorganic and organic compounds arises from the fact that in organic molecules all the electrons other than those in the bond under consideration participate in σ bonds, whereas in inorganic molecules lone electron pairs — s or also p electrons — are present, these being able to interact with the bonding electrons. To be sure, as long as only single σ bonds are present, as, for example, in the halogen molecules, ammonia or water, these lone pairs play only a subordinate rôle which can usually be left out of consideration, exactly as in the case of alcohols, amines, etc. in organic chemistry. But also in organic chemistry, the presence of such electrons may strongly influence the state of bonding when multiple bonds are to be found in the neighbourhood of an atom with lone electron pairs. It may then on occasions be necessary to take such a pair into consideration along with the electrons of the multiple bond in order to comprehend the state of bonding, as, for example, in pyrrole, furane³², and even in aniline and phenol³³. With the latter two, however, rather than the former, one may still be content with the usual structural scheme according to which the NH_2 and OH groups are linked by single bonds to a benzene nucleus, provided one does not wish to enter too far into the finer details of the state of bonding.

The great simplification which can be effected in the classification of bonds in organic chemistry thus rests upon the fact that the interaction

³⁰ For further, see W. KLEMM's *Magnetochemie*, p. 131.

³¹ Cf. footnote 38, p. 428.

³² W. HÜCKEL, *Theoretische Grundlagen der organischen Chemie*, Vol. I, p. 527 (6th Ed., 1949).

³³ *Ibid.*, Vol. II, p. 384 (5th Ed., 1948).

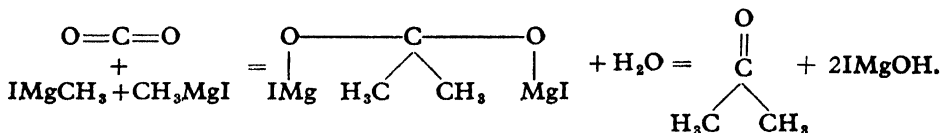
of lone electron pairs with bonding electrons does not normally need to be considered. In addition, the mutual influencing of the electrons operative in two different bonds can likewise be neglected in many cases. For σ electrons firmly accommodated in single bonds, this is immediately understandable, for the more loosely bound π electrons, however, not. But as soon as two multiple bonds are separated from one another by more than one single bond, it can be shown theoretically, in agreement with experience³⁴, that their π electrons do not interact with one another. If there is only one single bond inserted between them, however, so that a conjugated $C=C-C=C$ system is present, the interaction is then so considerable that it is no longer possible to consider each individual bond on its own: instead, the whole electronic system of the conjugated double bond is no longer reflected by the symbolic formula $C=C-C=C$. Such mutual influencing of neighbouring bonds is met with precisely in the case of small inorganic molecules containing only a few bonds.

Since in organic chemistry one has become accustomed to think of the individual bonds as in first approximation independent of one another, it is possible, wherever this supposition applies, to regard a whole list of properties as composed additively of parts which can be ascribed to the various bonds individually, wherein each kind of bond obtains its own characteristic value for each property. Mutual influencing of the bonds then makes itself noticeable in a deviation from the additive scheme. The best-known example is the recognition of a mutual influencing of bonds from a comparison of isolated and conjugated double bonds. With regard to molecular refraction, the conjugated double bonds exhibit relative to the isolated double bonds an — approximately constant — increase in the value for the molecular refraction, an *exaltation*, and in the heat of combustion a smaller value — the difference likewise being approximately constant. The magnitude of the deviation from the additive scheme may thus, to a certain extent, serve as a measure of the degree of mutual influencing of the bonds. Still stronger than in conjugated double bonds — for which the symbol $C=C-C=C$ nevertheless reflects satisfactorily some, even if by far not all, of the characteristics — is the mutual influencing of the double bonds in benzene. This has led to the aromatic state of bonding which prevails in it being represented by other formulae than that containing three double bonds due to KEKULÉ. These different formulae for benzene, where they are not simply manifestations of fantasy, represent attempts to distribute the valence electrons in different ways in the light of the electronic theory of valence. It is precisely in the case of conjugated double bonds that their chemical behaviour teaches that *one* formula does not suffice for an explanation of all the chemical reactions, but that for a clear description several are required with different

³⁴ There is however evidence that in compounds containing a $C=C-C-C=C$ chain, the central $C-C$ link is abnormally short: L. BATEMAN and G. A. JEFFREY, *Nature*, 1943, 152, 446; G. A. JEFFREY, *Proc. Roy. Soc.*, 1945, A 183, 388.

distributions of the valence electrons. Since, however, one particular state of a molecule, which will here be regarded as that poorest in energy, the ground state, must always be characterized by a particular distribution of electrons determined by the mean electron density at each point, this cannot be perfectly represented by all these different formulae.

If, now, with the help of the electronic theory of valence, it is desired to construct a "constitutional formula" for a simple inorganic compound, whose state of bonding cannot be directly associated with a particular bond formula, then several possibilities for distributing the electrons among the atoms and bonds usually result. In general, none of them corresponds completely to the physical and chemical properties. As a simple example, carbon dioxide will be discussed in detail. In order here to bring the four valencies of the carbon to expression, it will be formulated $:O=C=O:$ with two double bonds, in analogy to the organic compounds containing a carbonyl group. Since, however, here, otherwise than in the aldehydes and ketones, two double bonds radiate from the same atom, such a strong mutual influencing takes place that, physically as well as chemically, considerable differences relative to the carbonyl group are to be ascertained. The reactivity is strongly reduced, so that carbon dioxide does not respond to the ordinary carbonyl reagents. Under certain circumstances, it is true, it can react with GRIGNARD compounds as if it contained two carbonyl bonds. From CO_2 and CH_3MgI with subsequent hydrolysis it is possible to synthesize tertiary butyl alcohol $(CH_3)_3COH$ via acetone:



The acetone produced reacts more readily with the methyl magnesium iodide than does carbon dioxide, so that tertiary butyl alcohol is the main product formed. Physically, the difference between the carbonyl group in organic compounds and that in carbon dioxide is to be perceived among other things in the considerably reduced separation of the C and O in carbon dioxide. This amounts to only 1.15 Å³⁵ relative to 1.22 Å in aldehydes³⁶.

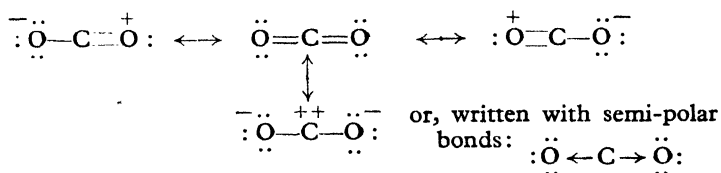
In place of the formula with two double bonds, which is accordingly not completely satisfying, it is possible to erect yet other formulae with different distributions of the electrons, for example, $:\overset{\cdot\cdot}{O}-\overset{+}{C}-\overset{\cdot\cdot}{O}:$. Since, however, the distance between singly bound carbon and oxygen is still greater, namely

³⁵ C. FINBAK and O. HASSEL, *Arch. Math. Naturvidenskab.*, 1941, 45, No. 3 (= *Chem. Abstracts*, 1942, 36, 6408), in good agreement with R. WIERL, *Ann. Physik*, 1931, [v], 8, 544 (1.13 Å — precisely as in ketene $H_2C=C=O$). In the lattice 1.13 Å: W. H. KEESOM and J. W. L. KÖHLER, *Physica*, 1934, [ii], 1, 167; 655.

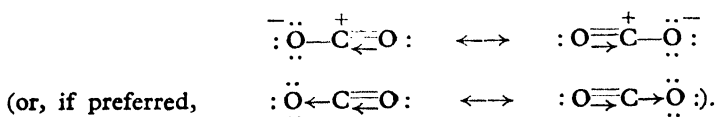
³⁶ D. P. STEVENSON, J. E. LUVALLE and V. SCHOMAKER, *J. Am. Chem. Soc.*, 1939, 61, 2508; D. P. STEVENSON, H. D. BURNHAM and V. SCHOMAKER, *ibid.*, p. 2922. Cf. p. 94.

1.43 Å, than in the carbonyl group, as far as the bond length is concerned it is even much less satisfying than the formula with double bonds. In it, in addition, the carbon appears to be surrounded by only two instead of four electron pairs, and would therefore be expected to incline strongly towards addition reactions, which is not the case. Further, it is also possible

to distribute the electrons unsymmetrically: $\overset{-}{\ddot{O}}-\overset{+}{C}\equiv\overset{+}{O}:$. However, such a distribution is in conflict with the absence of a dipole moment. Even with the help of the formal electronic theory of valence due to LEWIS and LANGMUIR, therefore, the true electron distribution in carbon dioxide cannot be illustrated by structural symbols. Since it lies, as it were, in a "mean" position between the stated structural-chemical electron distributions, one may speak after INGOLD³⁷ of a *mesomerism* of carbon dioxide. The different formulae by which the conceivable extreme cases of electron distribution can be considered as represented are termed limiting formulae. Mesomerism exists between these, and is indicated by the sign \longleftrightarrow inserted between them. In carbon dioxide, therefore, there exists a mesomerism between two symmetrical and two unsymmetrical limiting formulae* — two unsymmetrical because each of the two oxygen atoms can be regarded alternatively as the positive pole:



or, expressing the polar structure with a semi-polar bond:



The limiting formulae which can thus be written down for a compound have however yet another significance than that of reproducing the states of a molecule with particular limiting cases of electron distribution, *which in reality do not exist*, and with which one can at best conveniently illustrate certain reactions (as, for example, the previously mentioned reaction of CO₂ with GRIGNARD compounds). Proceeding from them, it is namely possible to calculate the electron distribution for the ground state of the molecule by a process of approximation. In this, one commences with the structures reproduced by the limiting formulae, for which the interaction between the π electrons can be given. These different interactions are superimposed upon one another in definite ways — not to be portrayed in greater detail here —

³⁷ C. K. INGOLD, *J. Chem. Soc.*, 1933, pp. 1124 and 1126.

* See translator's note, p. 434 ff.

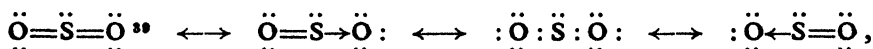
but not simply additively, so that there results for the ground state a charge distribution lying between all the structures. In this superimposing³⁸, not all the conceivable structures participate to the same extent. For example, in the forementioned example of carbon dioxide the structure : O=C=O :

certainly participates much more strongly than the structure : $\overset{-}{\ddot{O}}-\overset{++}{C}-\overset{-}{\ddot{O}} :$;

because the distance between C and O is much less for the doubly bound than for the singly bound atoms. This is certainly not the only possibility of arriving at the charge distribution in the molecule by calculation with an approximation procedure. There is also a second approximation procedure in which one first dispenses with all classical structural formulae and derives bond energies and charge densities of the electrons from the eigenfunctions of the atoms. Only subsequently does one find out which formula the calculated distribution most nearly approaches. Which of the two procedures can be the more expediently applied varies from case to case.

Express warning must be given here against an easily occurring error. In the participation of the individual structures in the ground state, one is not concerned with a material participation in the sense of an equilibrium. Only their weight in the formal execution of the approximation procedure is thereby meant.

The drawing up of inorganic structural formulae which are supposed to reflect the bonding relationships between the atoms thus has, on account of mesomerism, only a limited value, except when molecules containing nothing but single bonds are being dealt with. Actually, one must write down all the possible limiting formulae and link them up by the mesomerism sign, but even with this not much is gained as long as it is not known how strongly the individual limiting formulae participate in the ground state, or how far they correspond approximately to excited states which may be important for the behaviour of the molecule in reactions. Thus, for example, from the limiting formulae for sulphur dioxide, which may be written



it is never once possible to infer that the molecule has a bent structure. Nor can anything definite regarding its reactivity be gathered from them.

³⁸ This superimposing, after L. C. PAULING, is frequently denoted as *resonance* between the various structures, since an admittedly imperfect analogy exists between the coupling of mechanical systems and the superimposing of structures in the approximation procedure employed by PAULING. Since, because of the nature of this superimposing, it is liable to give rise to false conceptions, the expression will be avoided here. Cf. E. HÜCKEL, *Z. Elektrochem.*, 1937, 43, 763.

³⁹ This formula modelled on that for carbon dioxide permits the tetravalence of the sulphur to be recognized, but contradicts the octet theory. Nevertheless, this is no reason for not introducing it as a possible limiting formula, since in the case of sulphur, as an element of the second period, the octet theory does not have an unrestricted validity (p. 415).

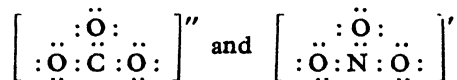
The possibility that the sulphur can become hexavalent follows in any case from its position in the Periodic System. One is already told more, however, if (in a space equivalent to that demanded by the limiting formulae) at least the dimensions of the SO_2 molecule are given:

$$\text{S-O distance } 1.45 \text{ \AA}, <\text{OSO } 124^\circ \pm 15^\circ, \mu = 1.60 \text{ D.}$$

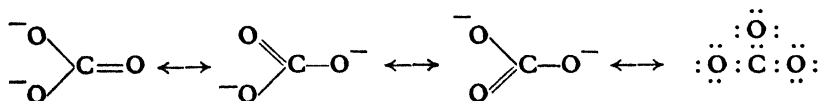
In the case of sulphur trioxide, the formula which, on advancing the rule that double bonds do not ordinarily occur among elements of the second period, is to be regarded as the limiting formula with respect to the electronic

theory of valence, $\begin{array}{c} \text{:}\ddot{\text{O}}\text{:} \\ \text{:}\ddot{\text{O}}\text{:}\ddot{\text{S}}\text{:}\ddot{\text{O}}\text{:} \end{array}$, does by all means indicate that, in consequence of the gap in the octet on the sulphur, the molecule will be capable of polymerization, this being able to lead to chainlike or cyclic structures. In addition, as for other compounds with the co-ordination number 3 which do not possess lone pairs of electrons, it could be predicted that the structure of SO_3 is planar. The dimensions of the molecule, which have been inferred from electron-diffraction experiments, can for the sake of completion be added by giving the $\text{S}\rightarrow\text{O}$ distance as 1.43 Å.

For the structures of the CO_3'' and NO_3' ions, there likewise results from the mesomerism concept a planar structure, which follows from the formulae



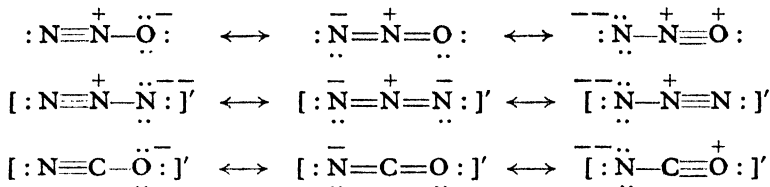
to be regarded as limiting formulae with a sextet on the central atom. They do not give the state of bonding exactly, however, since the unsymmetrical formula for CO_3'' with a double bond to the carbon (and analogously for NO_3') also participates in the ground state. Admittedly, the asymmetry of the ion does not become noticeable, since the unsymmetrical formula participates three times in the ground state, namely for each oxygen similarly:



These mesomeric formulae are supposed to indicate that the bond between the C and O in CO_3'' is not a simple semi-polar bond, but that a lone electron pair from each oxygen atom also participates in some way in the bonding, which corresponds somewhat to π electron bonding in a double bond.

The mesomerism which has been discussed in detail for carbon dioxide corresponds completely to that in nitrous oxide and the azide and cyanate ions, since CO_2 , N_2O , N_3' and NCO' are isosteric. Consequently it will suffice here if the limiting formulae are set down, between which the mesomerism exists*:

* Cf., in this connection, translator's note, p. 435.



The structure is in all cases linear ⁴⁰, as in that of carbon dioxide.

With respect to the individual cases, it still needs to be remarked that in nitrous oxide the sequence of the atoms is NNO and *not* NON. This has been inferred from the infra-red spectrum, which contains many more lines than that of carbon dioxide. Vibrations which are inactive in carbon dioxide appear in the spectrum of N₂O, whose symmetry must therefore be less. In contrast to CO₂, it cannot possess a centre of symmetry ⁴¹.

The almost total absence of a dipole moment — the measured value of 0.14 D lies close by the limits of error in the neighbourhood of zero — is no proof against the unsymmetrical structure of N₂O. Because of the mesomerism, an almost complete compensation of the differences in charge of the nuclei occurs through the structure of the electron cloud, exactly as in the cases of the “unsymmetrical” molecules NO and CO, for which similar small values are found for the dipole moments.

The structure of the azide ion permits an extensive equalization of the bonding relationships to be recognized, which places it in analogy to the very stable carbon dioxide molecule. For this stability, however, all the valence electrons present are collectively required. If, however, the N₃ group becomes homopolarly bound by an electron pair to an organic radical, the stability is lost. Organic azides are consequently explosive, as are also chlorazide, bromazide, and iodazide ⁴². It also suffices if the bonding in the lattice is not strictly heteropolar, as in the instances of the heavy-metal azides AgN₃ and Pb(N₃)₂ (where the metal atoms to some extent demand an electron pair for the bonding with an azide group), in order to give the substances a tendency to decompose explosively. In contrast, the heteropolar sodium azide NaN₃ evolves nitrogen on heating without exploding, and may consequently be employed for the preparation of very pure nitrogen.

The explosiveness apart, there exists a great similarity between azides

⁴⁰ N₂O and N₃' linear: V. SCHOMAKER and R. SPURR, *J. Am. Chem. Soc.*, 1942, **64**, 1184. Linear structure of N₃O from the molecular heat C_v at low temperatures: A. EUCKEN and E. DONATH, *Z. physik. Chem.*, 1926, **124**, 181. NCO' linear: S. B. HENDRICKS and L. C. PAULING, *J. Am. Chem. Soc.*, 1925, **47**, 2904; cf. also J. GOUBEAU, *Ber.*, 1935, **68**, 912. Mesomerism of NCO': N. V. SIDGWICK, *Trans. Faraday Soc.*, 1934, **30**, 801. The similarity in structure between NCO' and N₃' had already been inferred by J. A. CRANSTON and A. Y. LIVINGSTONE (*J. Chem. Soc.*, 1926, p. 501) by reason of the scarcely differing densities, refractive indices, solubilities and conductivities of cyanates and azides. N₃' in the ionic lattice of Sr(N₃)₂ linear, N—N distance, 1.12 Å: F. J. LLEWELLYN and F. E. WHITMORE, *J. Chem. Soc.*, 1947, p. 881.

⁴¹ E. K. PLYLER and E. F. BARKER, *Phys. Rev.*, 1931, [ii], **38**, 1828.

⁴² ClN₃: F. RASCHIG, *Ber.*, 1908, **41**, 4194. BrN₃: D. A. SPENCER, *J. Chem. Soc.*, 1925, **127**, 216. IN₃: A. R. HANTZSCH, *Ber.*, 1900, **33**, 522.

and chlorides in their solubilities — silver azide is deceptively similar to silver chloride — as well as between organic acid azides and acid chlorides. This similarity cannot be inferred from the limiting formulae — again a proof of their restricted usefulness — but can be from the electronic configuration if, after MULLIKEN, the electronic levels in the molecular ion N_3' are filled exactly as in the atomic ion Cl' . This is possible because, on the exclusion of the non-functioning electrons of the K shells, the N_3' ion possesses the same number — namely 16 — of valence electrons in the L and M shells as does the Cl' ion in the respective shells. To this must be added the fact that the size of N_3' is about the same as that of Cl' . There consequently occurs, as it were, an isosterism of higher order. According to this, N_3' would on the one hand be isosteric with CO_2 , and on the other with Cl' . In addition, silver cyanate $AgNCO$ is also similar to $AgCl$ in solubility and appearance. HN_3 is however an appreciably weaker acid than HCl . This must be attributed to a different interaction of the N_3' and Cl' ions with the water molecules, in which the linear structure of N_3' apparently plays a part, and in which the polar structures of N_3' possibly also assume an importance.

6. Mesomerism, Bond Types and Interatomic Distances

The limiting formulae between which mesomerism exists represent electron distributions with which the molecule would be richer in energy than it actually is in the ground state. They may correspond approximately — not perfectly, since several structures are invariably superimposed upon one another — to excited states which the molecule is able to assume. The bonding in the molecule is thus firmer than any one kind of bonding occurring in the limiting formulae would indicate. A firmer bonding corresponds to a closer approach of the nuclei of the atoms. In mesomerism, therefore, the atoms are closer than in the case of the bonds occurring in the limiting formulae. The mutual approach of the atoms on strengthening the binding is to be perceived on comparing the separation of singly, doubly and triply bound atoms for non-mesomeric compounds. For singly bound atoms of the first period the separation lies between 1.54 and 1.35 Å, for doubly bound between 1.35 and 1.2 Å, and for triply bound between 1.2 and 1.1 Å*. In this there is nothing like a continual transition, as might appear according to these numerical values comprising all kinds of atoms. Thus, if one considers the same atoms in single, double and triple bonding, the differences become very plain⁴³, as may be seen from the values given (in Å) in the following table:

* Cf., in this connection, translator's note, p. 436.

⁴³ The literature is for the most part to be found in W. HÜCKEL's *Theoretische Grundlagen der organischen Chemie*, Vol. II, p. 388 ff (5th Ed., 1948).

single bond		double bond		triple bond	
C—C	1.54 Å	C=C	1.34 Å	C≡C	1.2 Å
C—N	1.47	C=N	1.28	C≡N	1.16
C—O	1.43	C=O	1.22	C≡O	1.13
C—F	1.36 ⁴⁴				
N—N	1.47 ⁴⁵	N=N	1.23 ⁴⁶	N≡N	1.1
		N=O	1.22	N≡O	1.15
O—O	1.31	O=O	1.2		

The differences in the natures of the double and triple bonds, as they exist, for example, in O_2 and C_2H_4 , or in N_2 and C_2H_2 , are not here taken into account. Energetically speaking, which is again especially emphasized, the double bond is not twice, nor the triple bond thrice as strong as the single bond, for the single bond which, only slightly modified, is also contained in the other types of bonds is a σ bond, and is stronger than the π bonds which are effected by the more loosely bound π electrons, and which are added to it in the multiple bonds.

The influence of mesomerism, which decreases the interatomic distances, can be easily detected where, as in the examples given here, "normal values" can be given for the lengths of the uninfluenced bonds. This is shown very clearly by the example of carbon dioxide, which has already received a detailed discussion. Further, the diminution of the distance between carbon and nitrogen to 1.06 Å in the cyanide ion, to be compared with 1.16 Å in the CN group of nitriles, indicates that no ordinary triple bond is present in the cyanide ion (cf. pp. 420—421).

Where, however, as for the majority of elements of the higher periods, no compounds are known which contain uninfluenced bonds — *e.g.*, no compound is known with single or double sulphur-oxygen bonds — it is no longer possible to make inferences regarding mesomerism from interatomic distances or conversely. Yet the calculation of normal lengths has also been attempted for some of these bonds, for which, by halving the lengths in diatomic homopolar molecules, "atomic radii" have been derived, such being supposed in the case of normal unperturbed homopolar bonding to behave additively. The calculations carried out with these agree approximately in the case of organic compounds. This is likewise true in working

⁴⁴ In CF_4 . In CH_3F it is 1.42 Å.

⁴⁵ According to the compilation by H. A. SKINNER (*Trans. Faraday Soc.*, 1945, 41, 645) based on spectroscopic data. Here, however, O—O is given as 1.46 Å. Electron-diffraction measurements of N—N in gaseous N_2H_4 , 1.47 Å: P. A. GIGUÈRE and V. SCHOMAKER, *J. Am. Chem. Soc.*, 1943, 65, 2025; in symmetrical and unsymmetrical dimethylhydrazine 1.45 ± 0.03 Å: W. H. BEAMER, *ibid.*, 1948, 70, 2979. In crystalline $[N_2H_5]Cl_2$ and $[N_2H_5]F_2$ only 1.42 Å; here, two hydrogen bridges to the halogen ion exist, the $N_2H_5^{++}$ ion consisting of two inversely situated tetrahedra, thus having the symmetry D_{3d} : J. DONOHUE and W. N. LIPSCOMB, *J. Chem. Phys.*, 1947, 15, 115 (chloride); M. L. KRONBERG and D. HARKER, *ibid.*, 1942, 10, 309 (fluoride).

⁴⁶ 1.24 Å in azomethane $CH_3N=NCH_3$, according to H. BOERSCH, *Monatsh.*, 1935, 65, 311.

with atomic refractions, where the refraction values derived from the elements and from organic compounds approximately coincide. For the rest, very considerable deviations are to be found in part, as is indicated by the following tables:

atom	distance (Å)	radius (Å)	
H—H	0.74	0.37	In addition, the following atomic radii are given by PAULING and HUGGINS ⁵¹ , among others: B = 0.89 Å Si = 1.17 P = 1.10 S = 1.04
C—C	1.54	0.77	
O—O	1.31	0.65	
F—F ⁴⁷	1.45	0.72	
Cl—Cl ⁴⁸	1.98	0.99	
Br—Br ⁴⁹	2.28	1.14	
I—I ⁵⁰	2.66	1.33	

bond	calc. (Å)	found (Å)	com- pound	bond	calc. (Å)	found (Å)
H—F	1.05	0.92	BF ₃	B—F	1.61	1.30
H—Cl	1.38	1.28	BCl ₃	B—Cl	1.88	1.73
H—Br	1.51	1.41	SiF ₄	Si—F	1.89	1.54
H—I	1.70	1.6	SiCl ₄	Si—Cl	2.16	2.00
C—H	1.04	1.09	PF ₅	P—F	1.82	1.57
C—Cl	1.76	1.76	SF ₆	S—F	1.76	1.57
C—Br	1.91	1.91				

From the kind of agreement between calculation and observation, which in individual cases is excellent but in general is only very moderate, it may be concluded that the concept of "atomic radii" with respect to homopolar bonds is applicable in only a very limited sense. The deviations, which lie almost completely in such a direction that the observed lengths are smaller than the calculated, can be attributed to the fact that the lone electron pairs in such compounds participate more strongly in the bonding than in the compounds employed in the derivation of the standard values. Simply to denote this participation as mesomerism appears risky, since frequently, in

⁴⁷ L. O. BROCKWAY, *J. Am. Chem. Soc.*, 1938, **60**, 1348.

⁴⁸ In the crystal lattice 1.81 Å: W. H. KEESOM and K. W. TACONIS, *Physica*, 1936, [ii], **3**, 237; *Proc. K. Acad. Wetensch. Amsterdam*, 1936, **39**, 314.

⁴⁹ In the crystal lattice 2.27 Å: B. VONNEGUT and B. E. WARREN, *J. Am. Chem. Soc.*, 1936, **58**, 2459.

⁵⁰ In the crystal lattice 2.70 Å: P. M. HARRIS, E. MACK (Jr) and F. C. BLAKE, *J. Am. Chem. Soc.*, 1928, **50**, 1583.

⁵¹ L. C. PAULING and M. L. HUGGINS, *Z. Krist.*, 1934, **87**, 205. For H, 0.28 Å is given, and for F, 0.64 Å. These numbers have probably been obtained from the hydrogen halides by difference: H—Cl, 1.28, minus Cl, 0.99, gives 0.28; H—F, 0.92, minus H, 0.28, gives 0.64 — whereas otherwise the calculations with the hydrogen halides do not agree. W. GORDY (*J. Chem. Phys.*, 1947, **15**, 81) gives only 0.60 Å for the "covalent radius" of F, argued from the basis of the interatomic distances in the BeO and CaO double bonds (!) — indicative of how limited the applicability of covalent radii of this type is.

addition to a formula with single bonds, no reasonable second can be put forward as a limiting formula. Thus PAULING has tried to "explain" the reduction in length of Si—F, Si—Cl and similar bonds by saying that, as a consequence of the partial inclusion of a lone electron pair from the halogen in the bonding, the latter possesses "partial double-bond character". He even goes as far as expressing the fraction of such as a percentage⁵². Quite apart from the fact that it might be sceptically asked what is supposed to be gained by providing percentages of this sort, it does indeed appear possible, in the case of the elements of the second period, to construct a kind of double bond by filling the electron subgroups of the M shell of the central atom. In contrast, this is scarcely conceivable in the case of the planar boron halides. Here the lone electron pair from the halogen would have to enter partly into the gap in the octet of the boron atom. It is somewhat different when a lone electron pair enters into interaction with the π electrons of a double bond, as, for example, in vinyl chloride ClCH=CH₂. It is then fitting to speak of mesomerism as the cause of the reduction in bond length^{53*}.

⁵² PAULING does not calculate this percentage simply from the percentage diminution of the length or proportionately from the position of the observed value relative to those for single and double bonds, but according to an empirical function which he derives from the carbon-carbon distances in aliphatic, aromatic and unsaturated compounds and from graphite. See, in this connection, W. HÜCKEL's *Theoretische Grundlagen der organischen Chemie*, Vol. II, p. 392, footnote 4 (5th Ed., 1948).

⁵³ W. HÜCKEL, *Theoretische Grundlagen der organischen Chemie*, Vol. II, p. 390 (5th Ed., 1948). Certain investigators have turned against the idea that the reduction of the bond lengths in compounds such as SiF₄, SiCl₄, etc., is attributable only to double-bond resonance, including A. D. WALSH, *Trans. Faraday Soc.*, 1947, 43, 60; *J. Chem. Soc.*, 1948, p. 398; J. H. HILDEBRAND, *J. Chem. Phys.*, 1947, 15, 727; S. H. BAUER, *J. Am. Chem. Soc.*, 1947, 69, 3104. The latter writes: "It is evident that if interatomic distances are to be used as gages of bond order, tables of radii and methods of computation of separations to be expected for integral bond order must be clearly defined. . . I wish to argue that at the present stage of development of valence theory it is dubious whether this can be done. . . One can attach little significance to resonance schemes which purport to account for small deviations."

* *Translator's note.* — The theory of resonance or mesomerism, as developed and applied principally by PAULING during the 1930's, lies open to criticisms other than those mentioned by the author in the latter part of this chapter (p. 432 ff). Most fundamental of these is possibly the energetic aspect, which is far too often ignored or glossed over. According to the theoretical justification for the resonance concept, only limiting structures possessing the same or nearly the same energies can be regarded as making a significant contribution to the actual state of the molecule. Highly excited structures have a negligible effect and fall out of the picture. Yet, the extreme structures proposed to account for the bonding within molecules are frequently not even moderately close in their energies. This can be readily demonstrated for example, by continuing the discussion of the simple case of carbon dioxide originally selected by the author (p. 426 ff), for which compound PAULING (*The Nature of the Chemical Bond*, Cornell Univ. Press, 2nd Ed., 1945, pp. 195—197), writes: $\ddot{\text{O}}=\text{C}=\ddot{\text{O}}:$, $:\text{O}\equiv\text{C}-\ddot{\text{O}}:$ and $:\ddot{\text{O}}-\text{C}\equiv\text{O}:$ as the extreme structures. (The

approximate calculation which follows is in principle similar to that cited by PAULING, *op. cit.*, pp. 41—42 (footnote) for the example of the relative energies of the extreme homopolar and extreme heteropolar forms of the chlorine molecule. This type of treatment, which assumes point charges for the ions, is of course imperfect. It

results in exaggeration of the electrostatic energy at small distances through neglect of the fact that each ion possesses an exterior cloud of negative charge. For the sake of simplification, it is also neglected here that the observed interatomic distances are very far from the stablest equilibrium distances to be expected for the ionic structures. Correction for these factors would lead to an even greater destabilization of the ionic structures for resonance purposes than indicated by the ensuing considerations.) Granted that the sum of the energies of two double bonds will not differ greatly from that of one triple bond plus one single bond, the atomic heat of formation of $\text{O}=\text{C}=\text{O}$ on allowing one C and two O atoms to approach from infinite distance will be close to the atomic heat of formation of

$\text{O}=\text{C}=\text{O}$ from O^- plus C plus O^+ . But in view of the large difference between the ionization potential and electron affinity of oxygen, $\text{O}^- + \text{C} + \text{O}^+$ is richer in energy than $\text{O} + \text{C} + \text{O}$ by some 10.5 e-volt or 240 kcal, which figure still stands at about 110 kcal after taking into account the approach of the positive and negative charges to 2.53 Å — this distance representing the sum of the respective single and triple carbon-oxygen covalent bond lengths suggested by PAULING (*op. cit.*, p. 197)

after "correction" for the formal charges. The extreme structure $\text{O}^--\text{C}^+\equiv\text{O}$ is consequently less stable than the structure $\text{O}=\text{C}=\text{O}$ by approximately 110 kcal, which loss in stability is further reflected in the high oxygen-oxygen distance, this being considerably greater than twice the length of the ideal non-polar $\text{C}=\text{O}$ link (see p. 436).

It follows that one prerequisite for resonance, namely similarity in energy of the limiting structures, is here entirely lacking, and that the two $\text{O}^--\text{C}^+\equiv\text{O}$ structures

(still less $\text{O}^--\text{C}^+\equiv\text{O}$) make no significant contribution to the ground state. Yet PAULING (*loc. cit.*), in calculating the length of the bonds in CO_2 , assumes that the structures

$\text{O}^--\text{C}^+\equiv\text{O}$, $\text{O}=\text{C}=\text{O}$ and $\text{O}^+\equiv\text{C}-\text{O}^-$ participate *equally*, thus providing a completely erroneous presentation (cf. also A. BURAWOY, *Chemistry and Industry*, 1944, p. 434). Similar arguments can be levelled against the limiting formulae which have been proposed for a vast number of molecules, including those for nitrous oxide, the azide ion and the cyanate ion (cf. p. 430). Indeed, the number of instances in which, as in the cited case of CO_2 , the resonance concept has been employed in the scientific literature to give completely false pictures of the true state of bonding within molecules is virtually innumerable. It is no mark of erudition to write down a number of energetically impossible limiting formulae and connect them with the sign \longleftrightarrow in order to account for observed effects such as changes in bond lengths or dipole moments, especially when — as is frequently the case — other structures which are perhaps no more improbable must be tacitly excluded in order to avoid reversing the effect it is desired to "explain". To what misleading conclusions the resonance theory can and in fact frequently does lead — as well as its speculative nature — has been emphasized by A. BURAWOY (*Trans. Faraday Soc.*, 1943, 39, 79; 1944, 40, 537; *Chemistry and Industry*, 1944, p. 434; *Contribution à l'Etude de la Structure Moléculaire* (VICTOR HENRI memorial vol.), Desoer, Liège, 1948, p. 73). From a study of bond properties, BURAWOY concludes that the constitutive changes observed in covalent linkages, as well as their physical properties, depend upon a number of factors — including the variable screening of the nuclei by the electron systems and the polarizability of the latter — and cannot be described in terms of resonance among several valence-bond or ionic structures, the fundamental assumption involved, namely the existence of non-localized electrons, being in disagreement with a number of facts. Further objections to the resonance theory are also encountered by H. A. SKINNER and L. E. SUTTON (*Trans. Faraday Soc.*, 1944, 40, 164) in a comparison of the lengths of bonds involving halogen atoms in the partially halogenated derivatives of the methyl compounds of tin, arsenic and nitrogen, by S. H. BAUER (*J. Am. Chem. Soc.*, 1947, 69, 3107) in a comparison of the observed and predicted bond lengths of a number of halogen compounds, by A. F. WELLS (*J. Chem. Soc.*, 1949, p. 55) in a study of bond lengths of a wide range of inorganic molecules, including the anions of oxy-acids, and in particular by A. D. WALSH in his more extensive analysis of bond properties, which also makes use of the evidence supplied by ionization-potential data (see, among other places, *Trans. Faraday Soc.*, 1946, 42, 56; 1947, 43, 60; 158; *Discussions Faraday Soc.*, 1947, 2, 18; *J. Chem. Soc.*, 1948, p. 398; *Quart. Rev. Chem. Soc.*, 1948, 2, 73; *Ann. Rep. Chem. Soc.*, 1947, 44, 32).

Since the resonance theory cannot furnish a true picture of the bonding rela-

tionships in carbon dioxide, how then may this compound be represented? Obviously the form $O=C=O$ is by far the most stable of the classical formulae, and the ground state of CO_2 is best represented by $O=C=O$. There is however an important departure from the idealized formula. The bonding electrons are not equally shared by the atoms participating in the respective bonds, that is to say, the bonds are somewhat polar. Although the formula $O=C=O$ will serve for most purposes, the description cannot be regarded as complete as long as the polarity is not indicated — which can be simply accomplished (cf. L. H. LONG and A. D. WALSH, *Trans. Faraday Soc.*, 1947, **43**, 350) in less space than is required to write down the mesomeric forms frequently supposed to participate in the resonance picture. Should this be done, the variation in polarity of a bond, and hence the chemical significance of this variation, will not tend to be overlooked. It can be logically argued and supported by a wealth of experimental evidence (cf. WALSH, *op. cit.*), that — complicating factors being absent — the closer a bond approaches to the non-polar form, the shorter it becomes and the greater its stability. In principle, therefore, *the reactivity of a bond will decrease as the polarity decreases*. In this fact, then, is to be sought one of the reasons for the chemical inertness of carbon dioxide relative to other carbonyl compounds (cf. p. 426), the polarity of the $C=O$ bonds in CO_2 being much less than in aldehydes and ketones, for example.

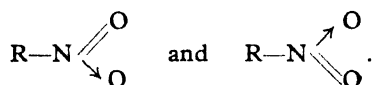
The lengths actually observed for bonds between unlike atoms are in no case "ideal" bond lengths, since all such bonds are inevitably more or less polar. The values quoted in the table on p. 433 are therefore in many cases appreciably longer than the values that would have to be attributed to idealized bond types. Thus, for example, an extrapolation of the variations in bond properties of the $C=O$ link indicates a length for the non-polar bond slightly shorter than in CO_2 (1.15 Å) and probably scarcely to be distinguished from the value observed in carbon monoxide (1.13 Å). (The idealized $C\equiv O$ triple bond, in which the bonding electrons are supposed to be shared equally between the two atoms, does not of course exist: but, in so far as it has any significance, the bond length must be considerably shorter than 1.13 Å — cf. BURAWOY, *Chemistry and Industry*, 1944, p. 435 — and possibly close to the value observed for the triple bond in the isoelectronic cyanide ion, namely 1.06 Å (cf. p. 432), there being a comparable similarity in bond length between NO^+ and N_2 , which are likewise isoelectronic.) Since the very low dipole moment eliminates the possibility that CO contains a highly polar triple bond, the evidence supplied by the bond length is unequivocally in favour of a double bond. In accordance with this, CO possesses just those bond properties one would expect for a nearly non-polar double bond (LONG and WALSH, *op. cit.*). Nor, again, is the resonance description — cf. PAULING, *op. cit.*, p. 135 — here applicable. To the objections mentioned by LONG and WALSH (*op. cit.*, p. 345), must be added

the further objection that the forms $\overset{-}{C}\equiv\overset{+}{O}$ and $\overset{+}{C}-\overset{-}{O}$, being of very different energy (on the basis of PAULING's bond lengths the former is about 100 kcal more stable than the latter), would participate to very different degrees in the "resonance hybrid". The pronounced dipole which would thereby arise is however not observed.

In molecules like vinyl chloride $ClCH=CH_2$, where a halogen atom is directly linked to a carbon atom participating in a multiple bond, the π electrons of the latter will doubtless be affected by the lone electron pairs belonging to the halogen atom (cf. p. 434). But, apart from energetic factors, there are various objections to describing this interaction in terms of resonance diagrams. These have been discussed by BURAWOY (*Trans. Faraday Soc.*, 1944, **40**, 538) and WALSH (*ibid.*, 1947, **43**, pp. 65 and 74; *J. Chem. Soc.*, 1948, p. 401).

The energetic objection to the resonance description, which exists wherever limiting structures of markedly different energy are under consideration, is however absent where equivalent forms are being dealt with, as in the case of the first three formulae indicated on p. 429 for the carbonate ion, and in the classical example of benzene. But even in the case of the latter molecule, the resonance theory does not explain why the change in bond length should bear the opposite sign to that normally observed for double bonds in other conjugated systems — see BURAWOY, *Contribution à l'Etude de la Structure Moléculaire* (VICTOR HENRI memorial vol.), p. 89. It may however be argued that it is these latter and not the benzenoid systems which are "anomalous" in this respect. Again, a study of additive molecular properties — molecular volume (through the parachor), molecular refractivity, dipole moment, bond lengths and bond strengths — over a wide range of compounds by R. SAMUEL (*J. Chem. Phys.*, 1944, **12**, 167; 180; 380; 521) points against the picture provided by the resonance description as being a true one, at least in the case of molecules frequently written with semi-polar double bonds, including nitro-

compounds which are often supposed to exhibit resonance between the two equivalent structures



If these are the *stablest* valence-bond structures that may be written, then the absence of resonance may be used as an argument against the relevance of the abstract concept of resonance to reality: but if, as suggested by SAMUEL, nitrogen is able to assume a covalency of five and form an entirely covalent structure of lower energy, then the facts are merely evidence against the applicability of resonance to the instances under discussion. SAMUEL sums up the general situation thus (*loc. cit.*, p. 522): "On the basis of the classical formulae we expect in first approximation constant and additive moments of the individual bonds, and we find them. On the basis of the resonance interpretation of the theory of the semipolar double bond we really cannot expect additive and constant bond moments, but we find them nevertheless. Hence we have to explain each of them by a whole series of fortuitous coincidences, which in the framework of the theory remain unexplained freaks of nature. . . It would appear that the classical concepts are superior by virtue of the principle of economy of hypotheses."

Enough has been said to indicate a serious need for a reply on the part of the advocates of the resonance theory to the various objections which have been raised in recent years. In the absence of a convincing response, the resonance theory stands in danger of being largely discredited, at least in so far as it has been applied hitherto. At best it provides a picture which can be described no less accurately in other terms. At worst, the picture it gives is highly misleading. It must further never be forgotten that the theory ultimately depends upon the use of limiting structures which, by admission, have no existence in reality. Much closer to reality is the concept of *bond polarity* latterly utilized and developed by WALSH, who has further suggested an appropriate symbolism (*Trans. Faraday Soc.*, 1947, **43**, 160 ff; 350). It need not be surprising, therefore, that the observed trends in bond properties can be much more satisfactorily interpreted in terms of the latter concept. That the polarity factor is not the only one governing variations in bond properties is however emphasized in their rather different approaches respectively by WALSH and by BURAWOY.

End of Volume I

In conformity with the Original, a comprehensive Author Index, Subject Index and Index of Elements and Compounds are provided for the work as a whole. In the present edition, these are to be found at the end of Volume II.

